The Chemical Degradation of Denture Soft Lining Materials: A Study of The Interactions Between Denture Soft Lining Materials And Food Simulating Liquids

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ABSTRACT

Denture soft lining materials are used as a cushion between the hard denture base and the oral mucosa. Fluid sorption and solubility may contribute to material hardening, roughening, cracking or tearing, loss of adhesion to the hard denture base or contamination by extrinsic stains or yeasts. The ideal material is required to have low fluid uptake, good wettability, retain compliance and surface integrity, and not support fungal growth. Evaluation of behaviour in the oral environment is difficult and a number of materials, such as artificial saliva and food simulating liquids, have been recommended to simulate the environment. The two types of denture soft lining materials commonly used in clinical practice are methacrylate and silicone based. These together with an experimental elastomer were evaluated in this study.

Fluid sorption and solubility were determined by immersion of disc specimens in food simulating fluids (distilled water, 3% acetic acid, 10% ethanol and 50% ethanol) and artificial saliva at 37±1°C with weighing at set time intervals. Similar experiments were carried out using liquids representing fatty food constituents with coconut oil and HB307. Hardness was determined using a Shore A durometer. In order to determine wettability, contact angle was measured using a computer microscope. The surface roughness was assessed using a non-contact laser profilometer. Finally, an attempt was made to identify leachable substances from the materials investigated using a Fourier transform infrared spectrometer. An additional part of this study was to look at the adhesion of one yeast species *Candida albicans* to commercial materials using various protective coatings to determine their efficacy.

The results demonstrated that the type of liquid simulating foods or artificial saliva, and immersion time significantly influenced the behaviour of the commercial denture soft lining materials and the experimental elastomer during *in vitro* testing. The two groups of materials behaviour were different. The two methacrylate-based denture soft lining materials showed marked absorption and solubility which may be associated with the loss of plasticisers. The two silicone-based denture soft lining materials showed much less absorption and solubility under the same conditions. The experimental elastomer showed marked swelling in oils, which was not expected, its chemical structure being similar to a methacrylate. Shore A hardness remained unchanged during the fluid immersion with the two silicone-based materials but showed measurable changes with the two methacrylate-based materials and the experimental elastomer, Increased surface roughness was also demonstrated with the two methacrylate-based materials, and decreased contact angle was found with the two silicone-based materials. After various surface treatment, coconut oil reduced *Candida albicans* adhesion in all cases.

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LIST OF ABBREVIATIONS

ANOVA	Analysis of variance
AS	Artificial saliva
ASTM	American Society for Testing of Materials
ATBC	Acetyl tributyl citrate
ATR	Attenuated Total Reflection
BCA	Bicinchoninic acid
BE	Bromo-butyl Butyl Elastomer
BEAS	Bromo-butyl Butyl Elastomer in unchanged artificial saliva
BECAS	Bromo-butyl Butyl Elastomer in changed artificial saliva
BECDW	Bromo-butyl Butyl Elastomer in changed distilled water
BECO	Bromo-butyl Butyl Elastomer in unchanged coconut oil
BEC10E	Bromo-butyl Butyl Elastomer in changed 10% ethanol
BEC3AA	Bromo-butyl Butyl Elastomer in changed 3% acetic acid
BEC50E	Bromo-butyl Butyl Elastomer in changed 50% ethanol
BEDW	Bromo-butyl Butyl Elastomer in unchanged distilled water
BEHB	Bromo-butyl Butyl Elastomer in unchanged HB307
BE10E	Bromo-butyl Butyl Elastomer in unchanged 10% ethanol
BE3AA	Bromo-butyl Butyl Elastomer in unchanged 3% acetic acid
BE50E	Bromo-butyl Butyl Elastomer in unchanged 50% ethanol
BPBG	Butyl phthalyl butyl glycollate
BP	Benzoyl peroxide
CASING	Cross-linking by activated species of inert gases
C. albicans	*Candida albicans*
CFU	Colony-forming units
CO	Coconut oil
D	Diffusion coefficient
DNBP	Di-n-butyl phthalate
DMPT	N,N-dimethyl -*p*-toluidine
DSLM	Denture Soft Lining Material
DST	Diagnostic Sensitivity Test
DW	Distilled water
E	Young's Modulus
EGDMA	Ethylene glycol dimethacrylate

EMA	Ethyl methacrylate
ES	EverSoft®
ESAS	EverSoft® in unchanged artificial saliva
ESCAS	EverSoft® in changed artificial saliva
ESCDW	EverSoft® in changed distilled water
ESCO	EverSoft® in unchanged coconut oil
ESC10E	EverSoft® in changed 10% ethanol
ESC3AA	EverSoft® in changed 3% acetic acid
ESC50E	EverSoft® in changed 50% ethanol
ESDW	EverSoft® in unchanged distilled water
ESHB	EverSoft® in unchanged HB307
ES10E	EverSoft® in unchanged 10% ethanol
ES3AA	EverSoft® in unchanged 3% acetic acid
ES50E	EverSoft® in unchanged 50% ethanol
FDA	United States Food and Drug Administration
FSL	Food simulating liquid
FTIR	Fourier Transform Infrared Spectroscopy
HB	HB307
HDL	High density lipoprotein
IIR	Isobutylene co-isoprene rubber
HPLC	High-pressure liquid chromatography
ISO	International Organisation for Standardisation
LP	Lauroyl peroxide
LDL	Low density lipoprotein
LPM	Laser profilometer
MB	Molloplast-B®
MBAS	Molloplast-B® in unchanged artificial saliva
MBCAS	Molloplast-B® in changed artificial saliva
MBCDW	Molloplast-B® in changed distilled water
MBCO	Molloplast-B® in unchanged coconut oil
MBC10E	Molloplast-B® in changed 10% ethanol
MBC3AA	Molloplast-B® in changed 3% acetic acid
MBC50E	Molloplast-B® in changed 50% ethanol
MBDW	Molloplast-B® in unchanged distilled water
MBHB	Molloplast-B® in unchanged HB307

MB10E	Molloplast-B® in unchanged 10% ethanol
MB3AA	Molloplast-B® in unchanged 3% acetic acid
MB50E	Molloplast-B® in unchanged 50% ethanol
MBDSLM	Methacrylate-based Denture Soft Lining Material
MCT	Medium chain triglyceride
MMA	Methyl methacrylate
***n*-BMA**	n-butyl methacrylate
PBMA	Poly(butyl methacrylate)
PBS	Phosphate buffered saline
PEGDMA	Polyethylene glycol dimethacrylate
PEMA	Poly(ethyl methacrylate)
PIB	Polyisobutylene
PDMS	Poly(dimethyl siloxane)
PMMA	Poly(methyl methacrylate)
PVC	Poly(vinyl chloride)
PVA	Poly(vinyl acetate)
R_a	Arithmetic roughness values
R_{max}	Maximum roughness depth
R_q	Root mean square roughness
RTV	Room temperature vulcanising
SAB	Sabourauds dextrose agar
SBDSLM	Silicone-based Denture Soft Lining Material
TEGDMA	Triethylene glycol dimethacrylate
T_g	Glass transition temperature
UTS	Ultimate tensile strength
VT	Vertex™Soft
VTAS	Vertex™Soft in unchanged artificial saliva
VTCAS	Vertex™Soft in changed artificial saliva
VTCDW	Vertex™Soft in changed distilled water
VTCO	Vertex™Soft in unchanged coconut oil
VTC10E	Vertex™Soft in changed 10% ethanol
VTC3AA	Vertex™Soft in changed 3% acetic acid
VTC50E	Vertex™Soft in changed 50% ethanol
VTDW	Vertex™Soft in unchanged distilled water
VTHB	Vertex™Soft in unchanged HB307

VT10E	Vertex™Soft in unchanged 10% ethanol
VT3AA	Vertex™Soft in unchanged 3% acetic acid
VT50E	Vertex™Soft in unchanged 50% ethanol
UG	Ufi Gel SC
UGAS	Ufi Gel SC in unchanged artificial saliva
UGCAS	Ufi Gel SC in changed artificial saliva
UGCDW	Ufi Gel SC in changed distilled water
UGCO	Ufi Gel SC in unchanged coconut oil
UGC10E	Ufi Gel SC in changed 10% ethanol
UGC3AA	Ufi Gel SC in changed 3% acetic acid
UGC50E	Ufi Gel SC in changed 50% ethanol
UGDW	Ufi Gel SC in unchanged distilled water
UGHB	Ufi Gel SC in unchanged HB307
UG10E	Ufi Gel SC in unchanged 10% ethanol
UG3AA	Ufi Gel SC in unchanged 3% acetic acid
UG50E	Ufi Gel SC in unchanged 50% ethanol
3AA	3% acetic acid
10E	10% ethanol
50E	50% ethanol

CHAPTER ONE

INTRODUCTION

In clinical dental application, the base of a complete denture is largely responsible for providing the prosthesis with retention, stability, and support by being closely adapted to the oral mucosa. The material most commonly used for denture bases is poly(methyl methacrylate) (PMMA). This rigid and hard material is used in the construction of prostheses in most edentulous patients because this material is highly durable. This is appropriate as long as the patients are in good health. However, as the number of elder people has increased, the oral condition of edentulous patients today appears to be different from that of 30 years ago. In particular, the alveolar and basal bone is highly resorbed, the oral mucosa is thinner, and the saliva flow and oral perception are deteriorating. A proportion of patients has become unable to cope with the hard material as the oral tissue becomes more fragile. Under these circumstances, to use denture soft lining materials to moderate the effects of forces of occlusion on the supporting tissue is highly desirable.

A denture soft lining material may be defined as "*a soft, elastic and resilient material forming all or part of the fit or impression surface of a denture*"(Wright, 1980a). It may act as a "cushion" (Kawano *et al.*, 1994a) between the hard denture base and the tissues to achieve a more equal distribution of the masticatory forces transmitted by the prosthesis to the underlying tissues. Various types of denture soft lining material such as natural rubber, plasticized acrylic, silicone rubber, and fluoro-elastomers have been developed for patients with chronic soreness of the soft tissues underneath the denture base (Craig and Powers, 2002). Unfortunately, there appears to be no definitive material to fulfil long-term clinical requirements in spite of reports of clinical durability of over five years having been noted (Wright, 1994; Braden *et al.*, 1995).

If the denture is successful in terms of comfort and functional effectiveness, the provision of a denture soft lining material will have meet the patient's expectations (Mäkilä and Honka, 1979; Schmidt and Smith, 1983a; Wright, 1994). It is possible to examine the lining extra orally where signs are visible of degradation including hardening, roughening, cracking or tearing, loss of adhesion, surface discolouring or contamination by yeasts. Patients however are generally unaware of the condition of the soft lining because of

visual and coordination impairment with ageing (Wright, 1984). It is important to determine what is meant by degradation in the context of this thesis. Here the term chemical degradation relates to changes in both properties and structure of the denture soft lining material associated with immersion in different solutions of chemical which simulate the oral environment.

Fig 1.1 Complete denture with a mandibular silicone rubber soft lining which has been in use for 10 years (adapted from Braden, Wright and Parker, 1995)

Hence, there are a number of clinical questions which need evaluation.

These include:

(1) What factors cause the material breakdown?

(2) What are the polymer-derived breakdown products?

(3) Does the material deterioration have any detrimental effects upon the individual's oral health?

(4) Does the length of service of soft-lined dentures appear to be adequate for routine clinical use?

CHAPTER TWO

LITERATURE REVIEW

2.1 Introduction

The main goal of dentistry is to maintain or improve the quality of life of the patient. The goal can be accomplished by preventing disease, relieving pain, improving mastication efficiency, enhancing speech, and improving aesthetic appearance. Because many of these goals require the replacement or alteration of existing tooth structure, the main challenge for centuries has been the development and selection of biocompatible prosthetic materials that can withstand the hostile oral environment.

Historically a wide variety of materials have been used as tooth replacements, including both animal and human teeth, seashells, ivory, bone, ceramic, gold, hydroxyapatite, cobalt-chromium alloy, and titanium. Materials for the replacement of missing portions of tooth structure have slowly and continuously evolved over the past centuries. In spite of recent improvements in the physical properties of dental materials, none of these are permanent. Dentists and materials scientists will continue the search for new materials for restorative dentistry. An ideal material is not available, and the inherent limitations of the material often lead to clinical failure. In seeking to predict the future, it is useful to look back at the past.

2.1.1 Historical Background

Dental disease has been a problem for humans for centuries. Dentistry as a speciality is believed to have begun about 300 B.C.. Egyptian tombstones indicated that tooth doctors were considered to be medical specialists. Gold bands and wires were used by the Phoenicians (after 2500 B.C.) and the Etruscans (after 800 B.C.) for the construction of partial dentures. The earliest documented evidence of tooth implant materials is attributed to the Etruscans as early as 700 B.C. In about 600 A.D. the Mayans used implants consisting of seashell segments that were placed in anterior tooth sockets. Hammered gold inlays and stone or mineral inlays also were placed for aesthetic purposes or traditional ornamentation by the Mayans and later by the Aztecs.

Modern dentistry is considered to have begun in 1728, when Pierre Fauchard (1678-1761), a French surgeon credited with being the "father of modern dentistry", published a

book, 'The Dentist Surgeon – A Treatise on Teeth', which effectively made public technical details of treatments and other procedures in dentistry, including a method for the construction of an artificial denture made from ivory (Anusavice, 1996).

As dental health improved, natural teeth were being retained until later life. Unfortunately, not all subjects were able to retain their teeth throughout their lifespan. When someone lost their teeth (became edentulous), they were likely to experience considerable difficulties in mastication and appearance. When dentures were first introduced during the 18th century, wax models of the mouth were used as templates from which ivory dentures were carved to the required shape. Dentures were difficult to construct, and considerable time and expense was needed. It was therefore mainly the rich who benefited from the provision of false teeth at this time.

By the latter part of the 18th century, lower ivory dentures inset with cadaver teeth worked relatively well and managed to stay in place, though there were difficulties with upper dentures which were usually a poor fit and were not retained so well. Upper dentures were thus later attached to lower dentures by means of springs or hinges to ensure they stayed in place. However, this led them to become heavier and cumbersome, tolerable for only short periods.

In 1756, Pfaff described a method for making impressions of the mouth in wax, and constructed a model replica with plaster of Paris. In 1792, de Chamant patented a process for the construction of porcelain teeth. The late 1700's was also associated with the first use of porcelain to make complete dentures or individual teeth. The need to mimic natural dentition with smooth surfaces and various colour shades was an important reason for considering porcelain as a dental material (Anusavice, 1996).

This situation was to change dramatically when dentures for the masses became available with the discovery by Charles Goodyear in 1850 of the process of vulcanisation. In this process rubber, when treated in the presence of sulphur, hardened to become vulcanite,

which is suitable for use as a denture base material (van Noort, 2002). Vulcanite was not only cheap, but also mouldable to fit oral structures.

In the 1950's came vast improvements with the introduction of the first of the synthetic acrylic resins (i.e. PMMA) that completely dominated the field, and continues to do so. The approach to treatment and the materials used in this treatment have evolved continuously, as the technique requires the prosthesis to be formed on an accurate positive replica of the recipient's mouth. Despite these improvements, many patients still experience difficulties in wearing or using dentures. In some cases, they may not be prepared to accept the limited efficiency of dentures when compared to the natural teeth they replace.

Changes in the occlusal surface and the continued bone resorption may result in the mucosal tissue under complete dentures becoming injured by excessive loads. Furthermore, the health of the tissue may deteriorate if denture hygiene is neglected. Under these conditions, the mucosal tissue may be rehabilitated by further corrective prosthetic treatment including the use of denture soft lining material which acts as a cushion to redistribute masticatory forces. In 1869, Twitchell used natural rubber as a denture soft denture lining material. However, this material became foul and ill-fitting, and also proved to have high water absorption. No other material was recorded until 1940.

Plasticised poly(vinyl chloride) (PVC) was one of the first synthetic resins to be used as a denture soft lining material (Matthews, 1945). Since 1958 (Lammie and Storer, 1958), silicone rubber material has been introduced as a denture soft lining material, and is still used today. The progress of materials, especially in polymers, drove the progress of modern dentistry.

2.1.2 Polymers

The term "polymer" comes from Greek: poly means "many" and mer means "parts". Polymers are organic materials characterised by long chain-like molecules built up from

many units (monomer). All atoms in a chain are bonded by covalent bond to each other, while Van der Waals bonding keeps the chains together. Polymers are a major constituent in all forms of everyday life including materials such as PVC and nylon are synthetic polymers. Cellulose, proteins, or even natural rubber, which is a poly(*cis*-1,4-isoprene) acquired from the *Hevea brasiliensis* tree, in the form of latex, are naturally occurring (http://www.chemheritage.org/EducationalServices/FACES/poly/readings/nat.htm).

In general, as the molecular weight of the polymer increases, the chains become longer and less mobile, resulting in increased strength, stiffness, and stability, giving a more rigid structure.

In addition to chemical composition and molecular weight, the physical or spatial structure may also influence the properties of the polymer. There are three basic spatial structures of polymers: linear, branched, and cross-linked (Figure 2.1). The linear polymers are produced where monomer units are joined together in single chains with two ends (Figure 2.1a). Branched polymers are those where branches extend outward from the main molecule (Figure 2.1b); Cross-linked polymers consist of adjacent linear chains that are joined one to another at various positions via covalent bonding (Figure 2.1c). Branched polymers form a class of polymers between linear polymers and polymer networks (i.e. between linear and cross-linked polymers). Branching and cross-linking will inhibit chain mobility, and highly cross-linked polymers may become very brittle, exhibiting little or no plastic deformation even at low rates of strain. Linear and branch molecules are discrete but are bonded to one another through weak, physical bonds. Upon heating, the weak bonds break and the chain mobility increases such that mobile chains may slide over or another resulting a softened material. Upon cooling, the bonds reform and hardening occurs. Materials that undergo this process are termed thermoplastic. Examples include PMMA, polyvinyl acrylics, and polystyrene. Cross-linking results in the formation of a network structure of covalently bonded atoms; primary linkages occur between chains, and the polymer actually becomes a single giant macromolecule. The spatial structure that allows chain sliding upon heating is not present in cross-linked materials. Cross-linked polymers therefore do not undergo softening upon heating and are

termed thermosets. Typical examples are silicones, *cis*-polyisoprene, and cross-linked PMMA (O'Brien, 2002).

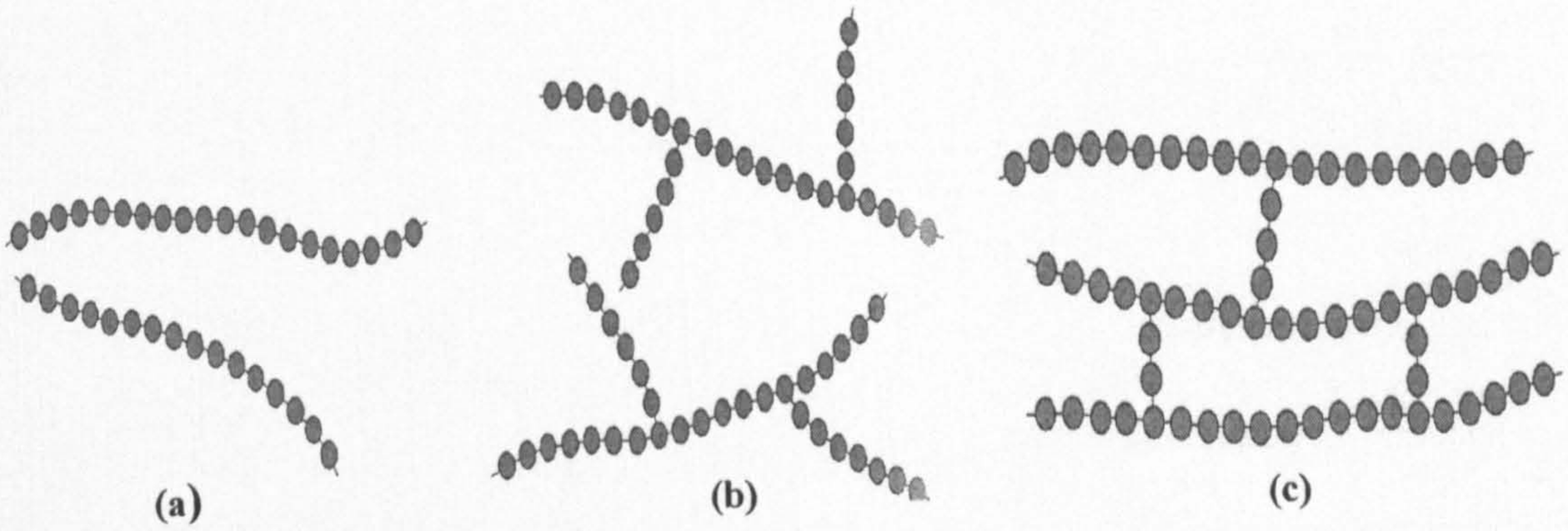


Figure 2.1 schematic representations of (a) linear, (b) branched and (c) cross-linked polymeric molecular structures (adapted from Callister, 2003).

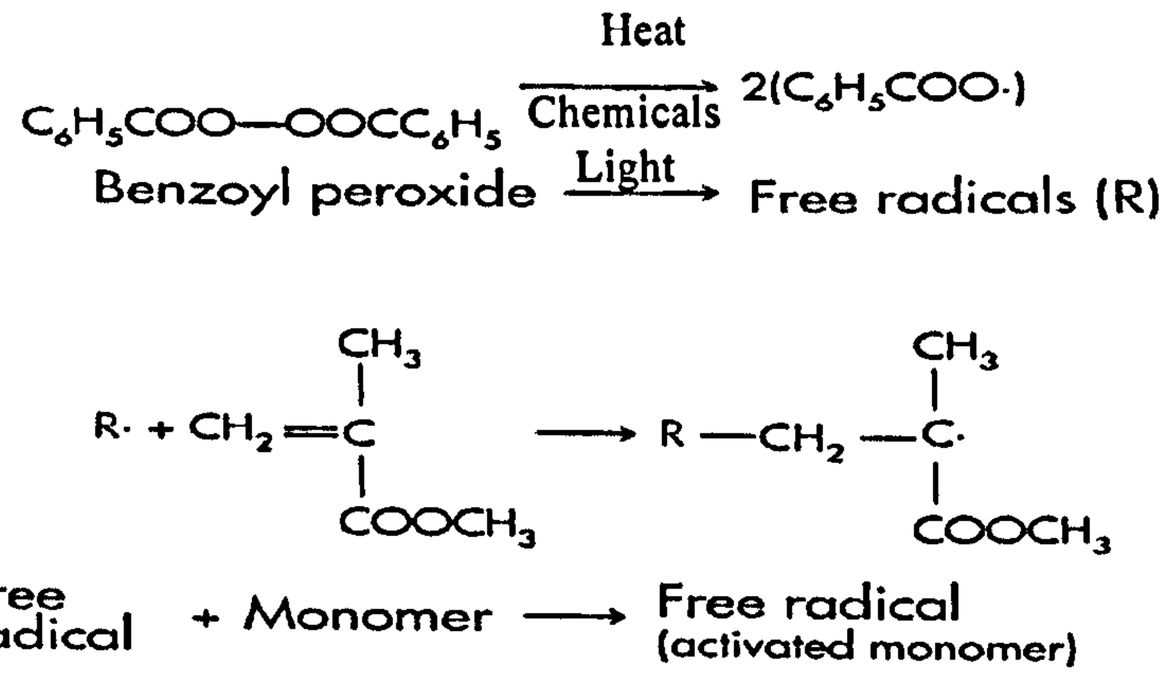
The polymerisation process may take place by several different mechanisms, but most polymerisation reactions fall into two basic methods: addition polymerisation, which monomers are added one after the other to make a long polymer chain, and condensation polymerisation; involves two molecules reacting together to form a larger molecule with the elimination of a by-product which is a smaller molecule (such as water or alcohol condensed out of the chemical reaction). Because of the production of by-products such as water or alcohol, these may evaporate and affect the dimensional stability of materials (Anusavice, 1996).

Unlike condensation polymerisation, addition polymerisation involves no change in composition, where the macromolecules are formed from smaller units, or monomers. Free-radical polymerisation is one type of addition polymerisation, which is a rapid reaction consisting of characteristic chain-reaction stages, namely, initiation, propagation, and termination.

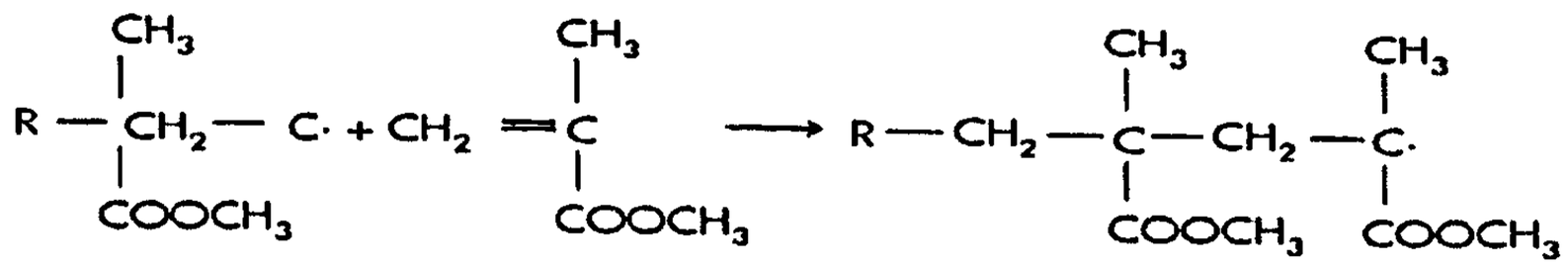
The three stages in the free-radical addition polymerisation reaction (Figure 2.2) are described as follows. They may be accelerated by heat, light, or small amounts of peroxides.

It is widely believed that polymerisation can only be initiated once the benzoyl free radicals have been produced. The radical reacts with the monomer, splitting the carbon-carbon double bond on the second monomer and transferring the free electron from the first monomer. The propagation stage continues with many monomers being added at a very rapid rate to create a chain molecule. As supply of monomer diminishes, the reaction enters the final stage where it terminates by the combination of the remaining free radicals. In some situations, there will also be some unreacted monomer consisting of just a few repeating units that become trapped within the polymer. These unreacted residual monomers can alter the toxicity and dimensional stability of the final polymer (Gebelein and Koblitz, 1981).

1. Initiation



2. Propagation



3. Termination

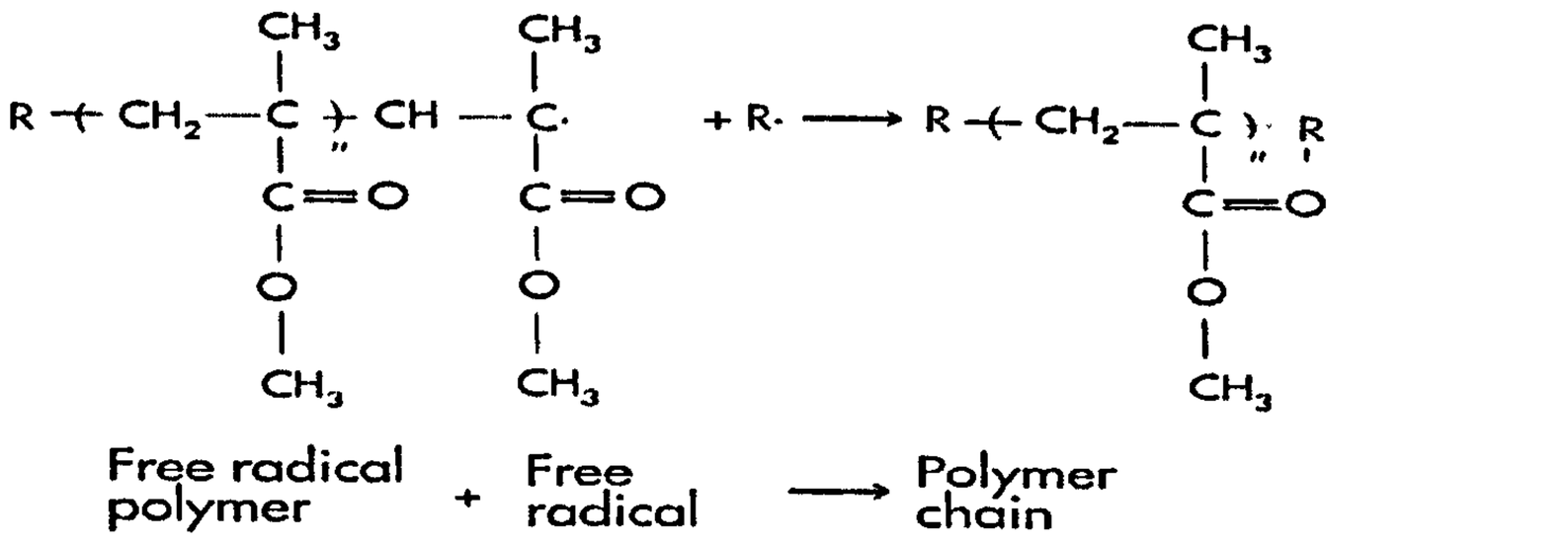


Figure 2.2 Three stages of addition polymerisation of methyl methacrylate (adapted from O'Brien, 2002).

2.1.3 Dental Polymers

Polymeric materials have a wide variety of applications in dentistry as denture bases materials; denture soft lining materials; resin composites; impression materials; custom trays for impressions; temporary restorations; maxillofacial prostheses; veneers and cements etc. They are easily processed in the laboratory, at the dental chair side, or in the oral cavity, and can be produced with near ideal aesthetics when required.

PMMA is the most important of the commercial acrylic polymers, and is used in very large quantities for full denture base fabrication and for adding soft tissue replica to cast metal frameworks. In modified forms, similar polymers may be used as denture soft lining materials.

Heat-cured polymerising PMMA is formed by a process of free radical polymerisation of the liquid monomer methyl methacrylate (MMA). Bulk polymerisation of MMA is carried out industrially to produce transparent plastics but this process would not be suitable for manufacturing dental appliances because the polymerisation of MMA itself results in a high volume shrinkage, and the reaction is highly exothermic. This would obviously result in gross dimensional inaccuracy and can result in temperature rise in excess of the monomers boiling point with consequent porosity. To avoid this, the dough technique was developed by Kulzer in 1938. This provided a viable means of processing using simple dental materials, and reduced volume shrinkage and exotherm. This was achieved by adding PMMA beads to the monomer (normal ratio used is 3:1 by volume of polymer to monomer) to form a saturated mix, in which polymerisation volume shrinkage is reduced from 21% to 7% since only approximately one third of the mix is monomer (Braden *et al.*, 1997). On initial mixing a consistency like wet sand is formed, followed after a short while by the string stage when thread-like beads of polymer, which adhere to the spatula, are produced. When the polymer loses tackiness and no longer sticks to the mixing spatula, the dough stage has been reached. This is the time at which the polymer is packed into gypsum-based moulds under pressure. Beyond this stage, the polymer becomes tough and rubbery, which is hard to manipulate (Braden *et al.*, 1997).

The powder principally contains the polymer beads, 35-200 μm in diameter, and within the beads there is usually residual benzoyl peroxide (BP) (0.5-1.5%) (an initiator). For denture bases, this powder is commonly mixed with a pigment for aesthetics and the monomer containing mainly MMA, and 0.1% hydroquinone (an inhibitor) to prevent spontaneous polymerisation on storage. Most denture base monomers contain 5-10% of a cross-linking agent (e.g., ethylene glycol dimethacrylate) (EGDMA) to improve hardness and wear resistance of the final product (Braden *et al.*, 1997).

MMA has a low latent heat, and hence is very much more volatile than might be expected. It also has a flash point well below room temperature, and thus should be handled well away from naked flames. Porosity is a real problem and must obviously be avoided because it can have a catastrophic effect on strength, dimensional stability, and oral hygiene of the denture (Ferracane, 1995). Decreasing the monomer/polymer ratio with an already polymerised material reduces exotherm, since gaseous porosity may be directly due to volatilization; moreover porosity can also result from the addition of too much powder in the dough mixture when MMA polymerises (van Noort, 2002).

Heat polymerising PMMA systems are powder/monomer systems, and heat is then required to decompose the initiator and polymerise the monomer. When heated above 65°C, the BP decomposes. This is the method used in the production of acrylic resin denture bases.

Room temperature polymerising PMMA systems are also powder/monomer systems; however, the monomer contains an activator to decompose the BP at room temperature. A common activator is N,N-dimethyl -*p*-toluidine (DMPT), 1-2.5% in the monomer, to breakdown the initiator. The initiation stage is characterised by a fast reaction between BP and DMPT, resulting in the production of free radicals.

2.1.4 Glass Transition Temperature (T_g) and compliance

The glass transition temperature (Figure 2.3) is the temperature at which a polymer experiences a significant change in properties. At sufficiently low temperatures all

polymers are hard, rigid solids. As the temperature rises, polymer chains gain in thermal energy enabling them to move more freely relative to each other. Thus, the T_g marks the onset of segment mobility for the polymer. From a practical point of view, the value of T_g has great significance. For example, for materials required to stay rigid in the mouth (e.g., denture base materials, it is ideal to have the T_g well above temperatures experienced in the mouth to avoid distortion. PMMA is the hardest resin of the series with the highest T_g. Poly(ethyl methacrylate) (PEMA) possesses a lower T_g and poly(butyl methacrylate) (PBMA) has an even lower T_g (Figure 2.4).

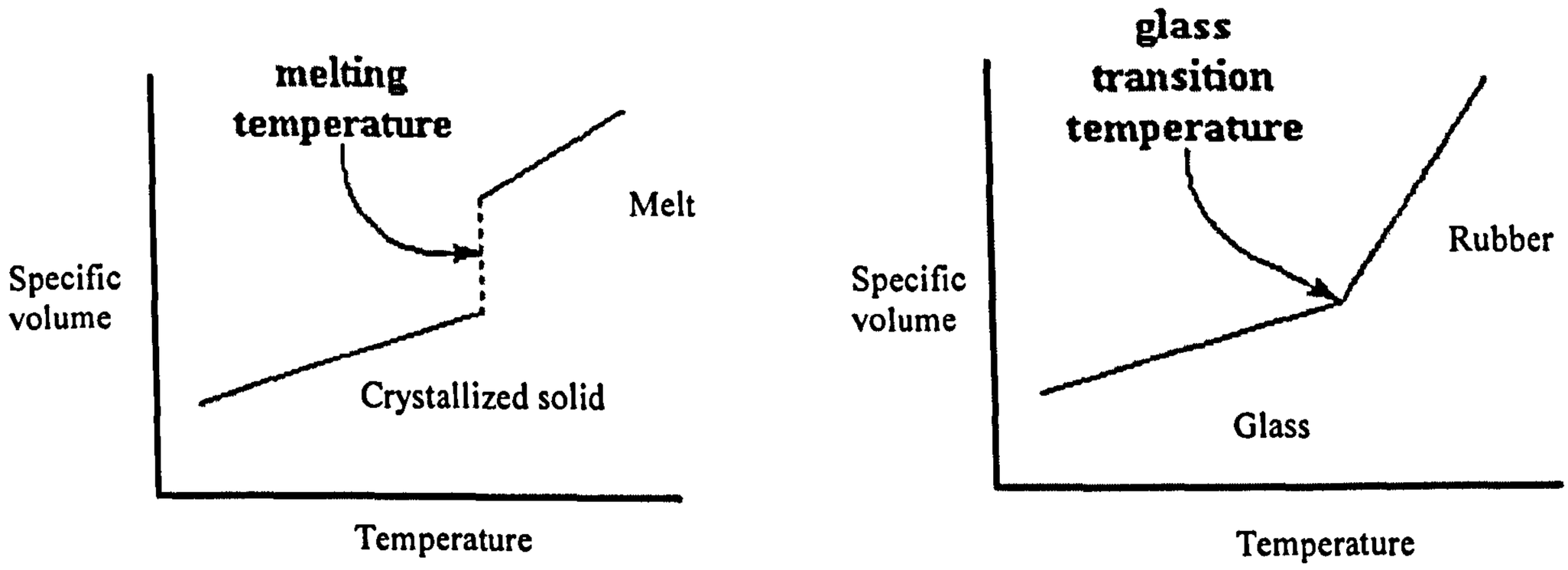


Figure 2.3 A specific volume vs. temperature plot, for a crystalline polymer, on the left; and an amorphous polymer on the right (adapted from http://faculty.uscs.edu/1lever/polymer%20Resources/GlassTrans.htm).

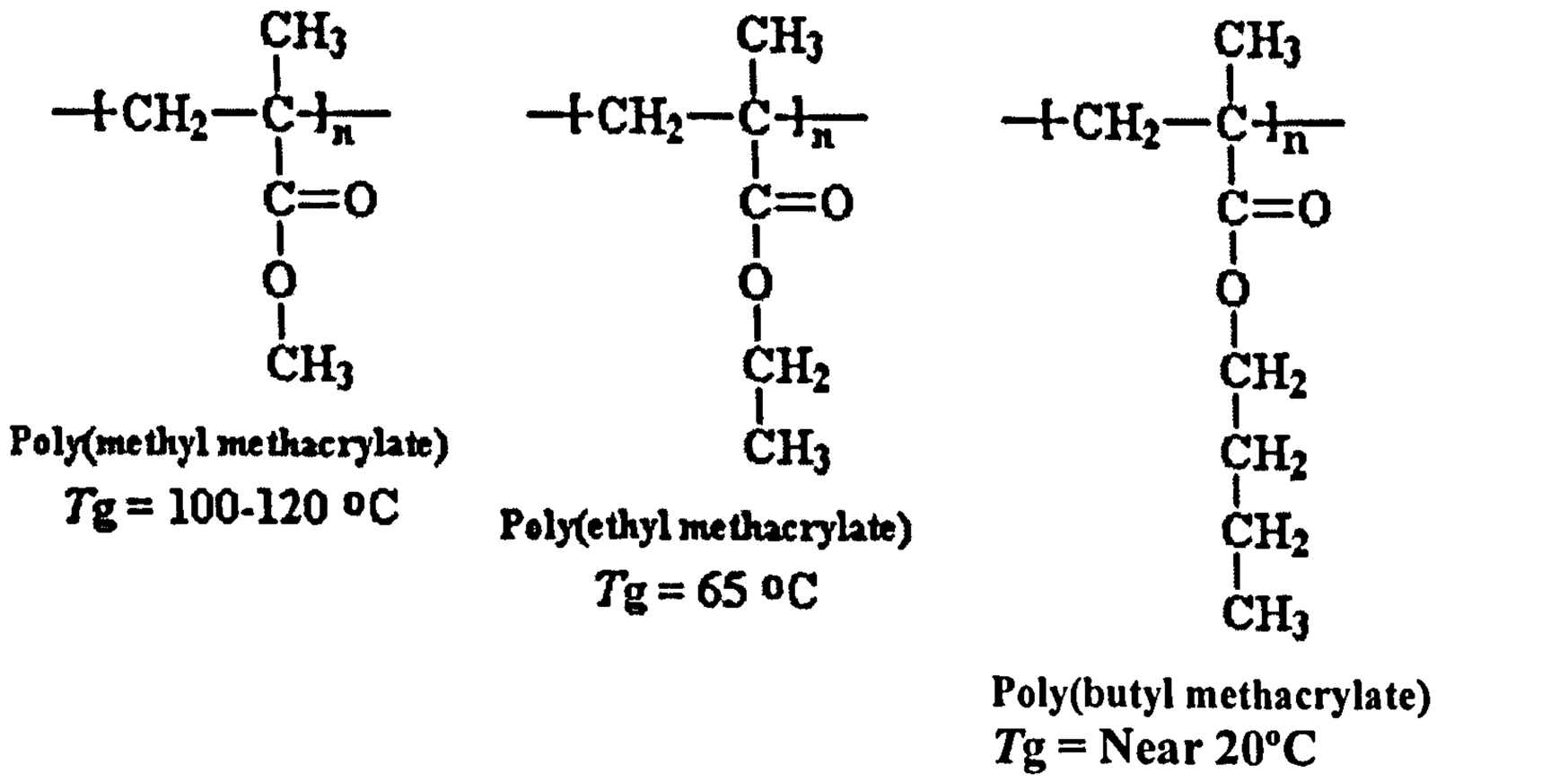


Figure 2.4 Molecular structure and glass transition temperature (T_g) of some methacrylate polymers (adapted from http://pslc.ws/macrog/tg.htm).

Side groups attached to the main chain backbone have an equally large influence associated with their bulkiness and effect on packing. Side groups generally tend to create more free volume by disrupting the packing of the main chain and thus lowering the T_g. Table 2.1 shows the T_g of a number of n-alkyl methacrylates whose esters contain 1, 2, 3, 4 and 6 carbon atoms. A clear trend is observed as the higher methacrylates have progressively low T_g.

Table 2.1 Relation between Tg and side groups in the methacrylate family (adapted from Braden *et al.*, 1997)

n-alkyl methacrylates	Methyl (1C)	Ethyl (2C)	Propyl (3C)	Butyl (4C)	Hexyl (6C)
T_g(°C)	115	62	38	27	-5

The softness of the material when it is deformed may be more correctly described as its compliance, which is the reciprocal of the elastic modulus, i.e. strain/stress (Wright, 1980a; Graham *et al.*, 1990). The elastic modulus represents the stiffness of a material within the elastic range. The stronger the interatomic or intermolecular forces of the material, the greater the values of the elastic modulus and the more rigid or stiff the material (Craig and Powers, 2002).

Those materials required to be compliant (e.g., denture soft lining materials) must have a T_g below or at mouth temperature, so that they are in their rubbery state at mouth temperature, to function effectively. The T_g of the polymer will reduce when a plasticiser is added in the monomer. If enough plasticiser is added, a brittle polymer can be transformed into a soft, flexible polymer. PEMA is used as the powder of denture soft lining materials because it has a lower T_g than PMMA and hence requires less plasticiser. These methacrylate-based denture soft lining materials have the advantage that they bond well to the PMMA denture because of similar chemical composition. However, the drawback is that the plasticiser gradually leaches out leading to the material loosing its compliance.

2.1.5 Silicone rubber

2.1.5.1 Introduction

Since the 1960s, silicone rubber has found widespread use in medical, aerospace, electrical, construction, and industrial applications. Flexibility over a wide temperature range, good elastic recovery, damping effect, and inert and stable compounds are among the reasons for its popularity. Common silicone medical components and assemblies include airways, balloon catheters, tubing for feeding, breast implants, urinary catheters, voice box prostheses, intraocular lens, dental impression materials, denture soft lining materials and maxillofacial prostheses.

Silicone rubbers are synthetic polymers with an unusual molecular structure—a giant backbone of alternating silicon and oxygen atoms. This structural linkage is similar to that found; for example, in a mineral such as quartz, and silicones have superior heat resistance compared with other elastomers.

2.1.5.2 Properties of silicone rubber

Unlike other elastomers, which have carbon-carbon backbones, silicone rubbers contain very flexible siloxane backbones, and have a naturally low glass transition temperature. The most commercially popular and widely used silicone rubber is poly(dimethyl siloxane) (PDMS). The methyl groups attached the backbone of Si-O-Si chain give the polymer its characteristic properties which are biocompatibility, superior temperature and chemical resistance, good mechanical and electrical properties (Heide, 1999).

2.1.5.3 Chemistry of silicone rubber

In general, the convenient way to distinguish various types of silicone rubbers is dependent on their curing reaction. There are three main ways they may be cured (Rochow, 1987);

1. Condensation curing: the material cures by the reaction of a catalyst (usually an organo tin) on siloxane chains end terminated with alkoxy and hydroxyl groups with the evolution a volatile alcohol. This type is used in dentistry.

2. Addition curing: there are two types of addition reaction, hydrosilyation and peroxide curing. In dentistry, these types are widely used in impression materials because of their dimensional stability and accuracy.
3. Acetoxy curing: this is dependent on water penetrating the matrix of the material to initiate the curing reaction with the evolution of acetic acid. This type is rarely used in the mouth because of its by-product.

2.1.5.3.1 Condensation curing silicone rubber

Condensation curing silicone rubber is a room temperature vulcanising (RTV) silicone rubber. It is hydroxyl terminated PDMS crosslinked with an alkoxysilicate initiated by organo tin catalyst (e.g., tin octoate) (Figure 2.5).

The cross-linking reaction in Figure 2.5 occurs with elimination of alcohol, volatilization of which can contribute to lack of dimensional stability. Moreover, their hydrophobic nature also limits its use in the mouth. Hence, this type of material is not an ideal denture soft lining material.

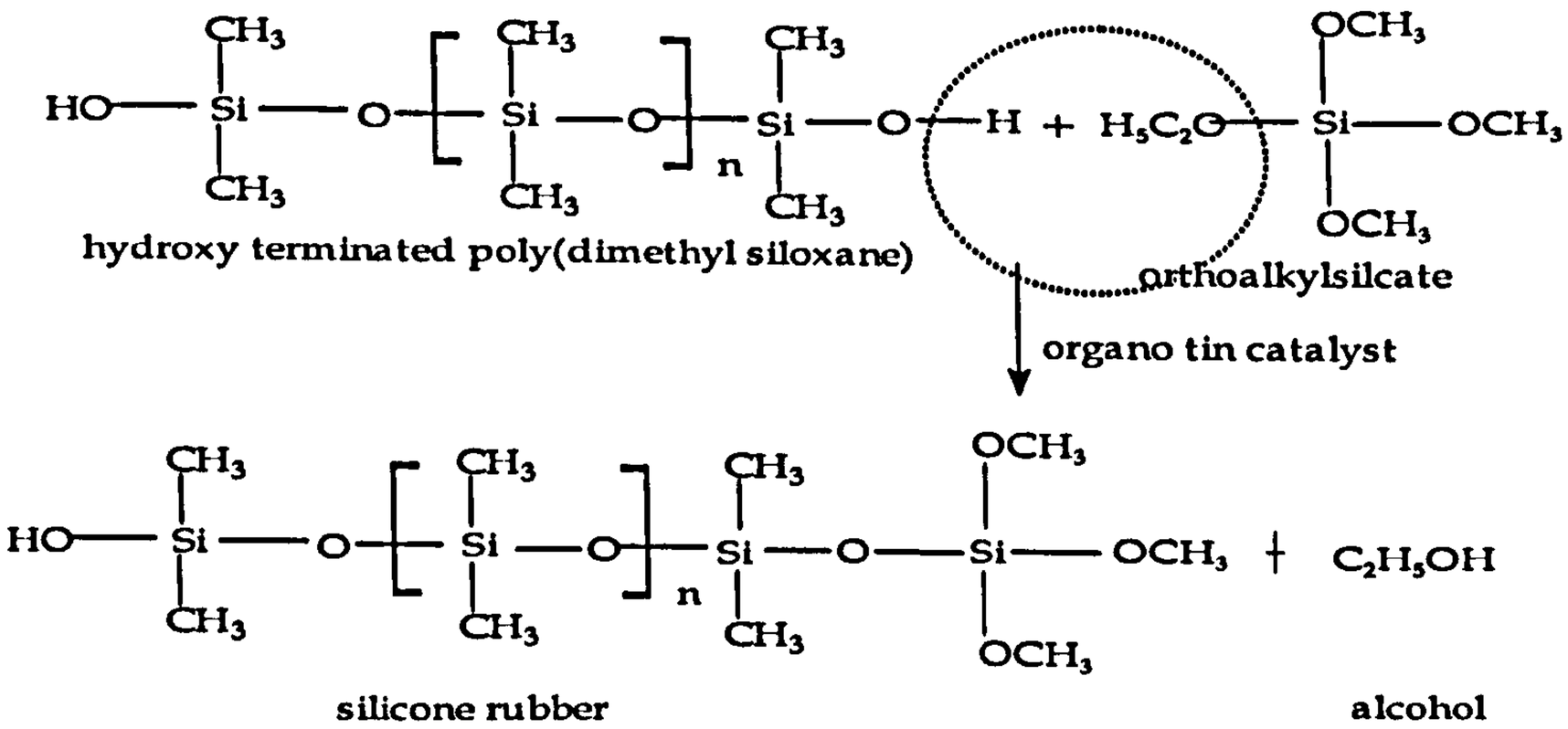


Figure 2.5 Typical condensation curing reaction (adapted from O'Brien, 2002).

2.1.5.3.2 Addition curing silicone rubber

2.1.5.3.2.1 Hydrosilanised curing silicone rubber

Hydrosilanised curing silicone rubber is a type of addition RTV silicone rubber. The addition reaction occurs by the linking of Si-CH=CH_2 with Si-H and results in Si-CH_2-CH_2-Si. This end group reaction is catalysed by the presence of a platinum complex

(Figure 2.6). Crosslinking increases the viscosity of the silicone and develops the elastic properties. The amount of reaction is determined by the relative ratio between the vinyl and H-terminated siloxane. These materials are available in two-paste system (1:1 ratio) or auto-cartridge form for use by dental practitioners.

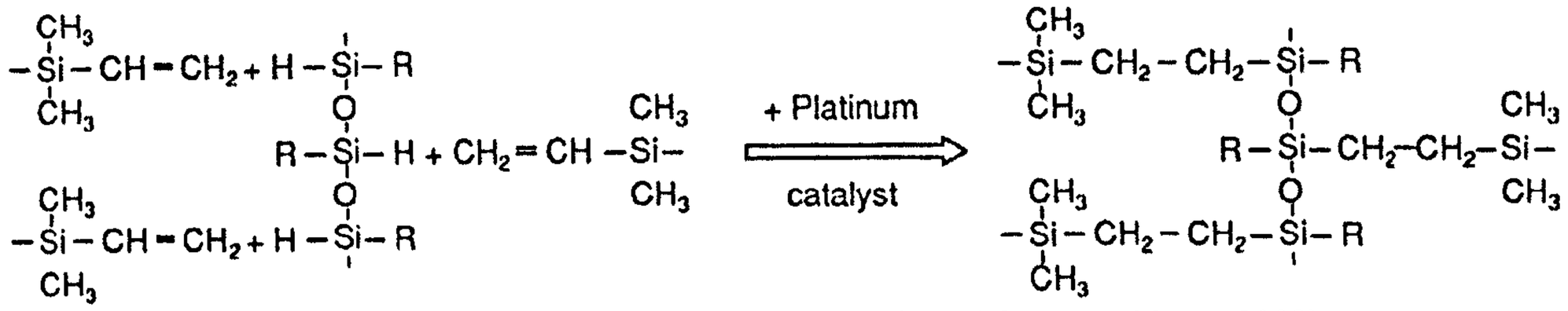


Figure 2.6 Hydrosilanation curing reaction (adapted from van Noort, 2002)

The platinum catalyst is typically chloroplatinic acid and the mechanism for the catalyst to polymerise the silicone has been shown by Riggs (1997) (Figure 2.7).

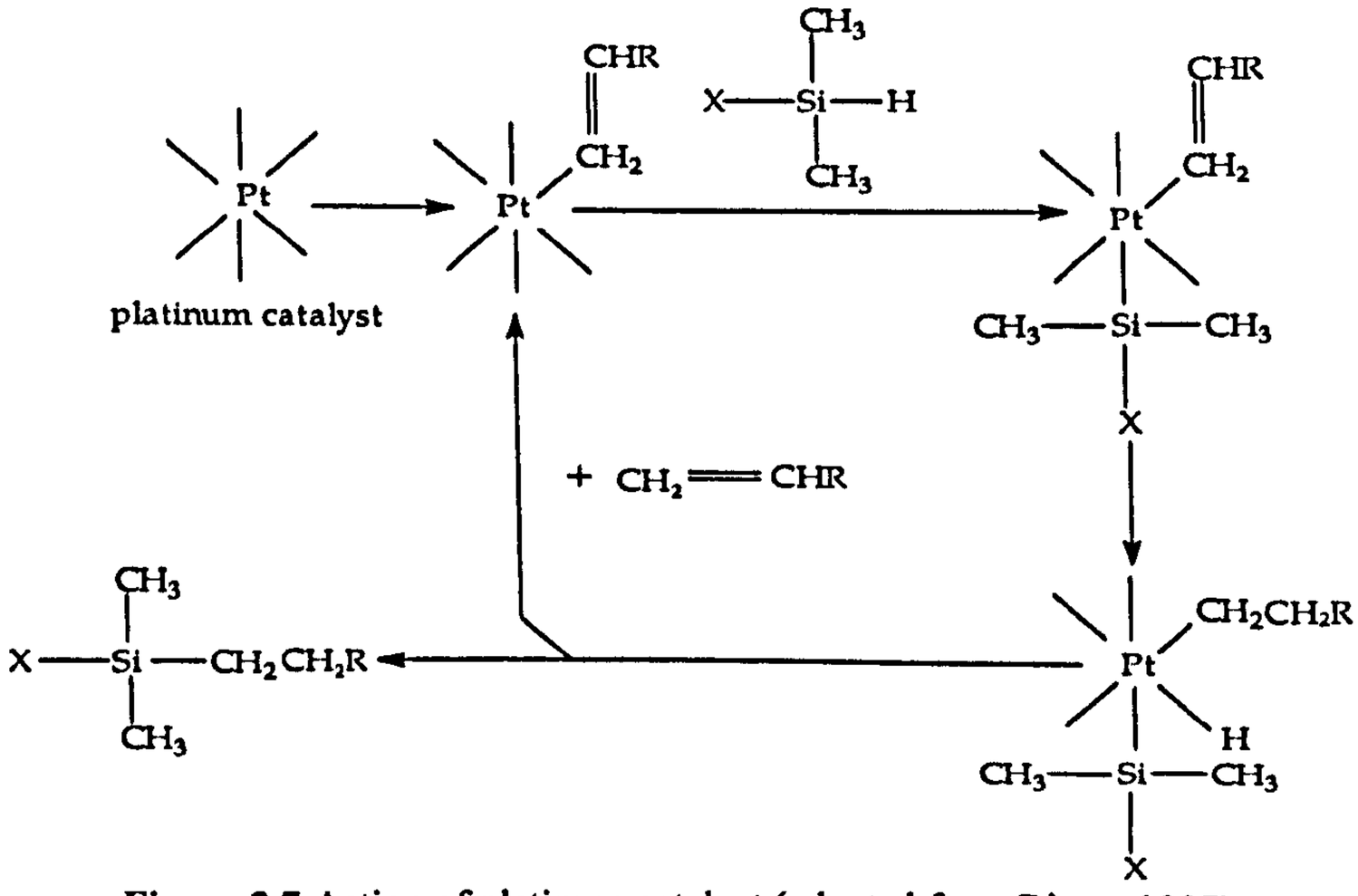


Figure 2.7 Action of platinum catalyst (adapted from Riggs, 1997).

2.1.5.3.2.2 Peroxide curing silicone rubber

The peroxide curing silicone rubber uses a free radical to initiate the oxidisation of CH_3 groups on neighbouring chains to form Si-CH_2-CH_2-Si crosslinks between the chains (Rochow, 1987). In dental materials, the most familiar initiator would be benzoyl peroxide. During the process, oxygen is released as the peroxide starts to decompose.

Peroxide curing silicone rubbers are largely formulated as one-paste systems because they are more stable at room temperature than condensation curing silicone rubbers.

In both types the addition silicone is more suitable as a denture soft lining material than the condensation silicone because there are no by-products. However, silicone rubber does not bond readily to the acrylic resin of the denture, so an adhesive needs to be employed. This adhesion can be achieved using silicone dissolved in a solvent, or by the use of an alkyl-silane coupling agent. However, this is not ideal. Another drawback is that this material tends to support the growth of *Candida albicans*, which leads to denture related stomatitis (van Noort, 2002).

2.2 Denture soft lining materials

2.2.1 Ideal properties of denture soft lining materials

For maximum clinical durability, denture soft lining materials should display the following properties (Wright, 1980a; Qudah *et al.*, 1990):

1. They should be non-toxic, odourless, and non-irritant to encourage long-term use of the denture by the patient.
2. They should be easily processed and no dimensional change should occur during processing.
3. They should retain compliance in order to remain soft enough for the comfort of the patient. The degree of compliance will depend on the chemical composition of the material and the thickness of the soft lining. Several authors suggest that thicknesses of between 2 and 3 mm are most appropriate to provide suitable compliance for clinical use (Wright, 1976; Kazanji and Watkinson, 1988b).
4. They should bond sufficiently well to PMMA to avoid separation during use. If the strength of the adhesion between the two materials is weak, interfacial separation takes place easily during use. Bonding failure between the lining material and the denture base can create an environment for potential bacterial growth and accelerated breakdown of the denture soft lining material (Jacobsen *et al.*, 1997).

5. They should have low water absorption and solubility. High absorption and solubility of the denture soft lining materials are generally associated with swelling, distortion, hardening, absorption of odours, support of bacteria, colour changes, and debonding of denture soft lining materials from the denture base. Therefore, sorption properties are important as a means to evaluate the longevity of a denture soft lining material (Kawano *et al.*, 1994b).
6. They should have sufficient mechanical strength, abrasion resistance and tear resistance to resist damage and prevent rupture while in the oral cavity or during cleaning.
7. They should inhibit fungal growth.
8. They should have good surface wettability to ensure that the surfaces are adequately lubricated by saliva to prevent frictional trauma.
9. They should be easy to clean and not affected by foods, drinks, and denture cleaners.
10. They should be possible to adjust and polish to produce a sufficiently smooth surface in comparison to a hard denture base.
11. They should be aesthetically acceptable and their colour should match that of the denture base material.

2.2.2 Disadvantages of denture soft lining materials

2.2.2.1 Cost

The time-consuming expense of any prosthesis incorporating a denture soft lining material is greater than that of the same denture constructed of only a single base material. Also, the more frequent replacement of the denture soft lining material due to degradation, the more the life time expense.

2.2.2.2 Problems in fabrication

The fabrication of commercial long-term denture soft lining materials often involves complex and time-consuming laboratory procedures, greater than for a simple denture. Some denture soft lining materials may be processed at the chairside, but this group has tended to be less stable and shown a shorter clinical life than those processed in the

laboratory. Also, how to get a uniform thickness of chairside denture soft lining material is still a task in chairside practice.

2.2.2.3 Problems in adjustment, polishing, and repair

All denture soft lining materials are difficult to adjust or modify. They present problems in polishing, especially of the acrylic detail at the junction between the rigid base and the soft polymer lining. All varieties are complex to repair if fracture or other damage occurs to either the hard base or the soft polymer lining.

2.2.2.4 Fracture of the supporting denture base

The provision of a soft lining for a denture inevitably reduces the bulk of acrylic on which the prosthesis is dependent for its overall rigidity and strength. The most characteristic consequence of this reduction in acrylic mass is early fracture of the denture (Mäkilä and Honka, 1979).

2.2.2.5 Fungal colonisation

Fungal colonisation of denture soft lining materials is well documented (Storer, 1962; Mäkilä and Honka, 1979; Wright, 1980b; Schmidt and Smith, 1983b). Poor denture hygiene leads to an increased probability of colonisation of *Candida albicans* or other species of *Candida* on the fitting surface of soft lined mandibular dentures (Wright *et al.*, 1985). Burns *et al.* (1987) suggested that some denture soft lining materials promote the growth of *Candida albicans* in vitro, while Graham *et al.* (1991) reported that two denture soft lining materials supported the presence and growth of oral yeast. Moreover, the increased porosity of denture soft lining materials can lead to plaque accumulation and *C. albicans* colonisation (Nikawa *et al.*, 1994). In general, colonisation may reduce the intra-oral life of the soft lined denture (Wright *et al.*, 1998).

2.2.2.6 Changes in dimensional stability

Some denture soft lining materials are inherently dimensionally unstable. Water absorption and plasticiser loss lead to a continuing variation and change during intra-oral wear (Lammie and Storer, 1958; Storer, 1962; Wright, 1976; Braden and Wright, 1983).

From the clinical view point, changes in dimensional stability will affect the tissue surface and vertical dimension and lead to loss of accuracy of fit.

2.2.2.7 Changes in surface integrity

The surface integrity of many long-term denture soft lining materials appears to be less stable than might be expected. Microscopic surface fractures, or even macroscopic cracking has been reported by several researchers. (Suchatlampong *et al.*, 1976)

2.2.3 Clinical failures of denture soft lining materials

2.2.3.1 Loss of compliance

The condition of the oral load bearing tissues may be adversely affected by high stress concentrations during function especially for denture patients with diabetes or other debilitating diseases and for many geriatric patients. Soft lined dentures are especially preferred for the over-sensitive mucosa.

Loss of compliance in the oral environment has most often been reported with plasticised acrylic materials because of the susceptibility of the plasticiser to leach out of the material (Braden *et al.*, 1995). Conversely, silicone rubber materials have frequently been reported to maintain their compliance over a long period of time (Mäkilä and Honka, 1979; Schmidt and Smith, 1983a; Wright, 1984) due to their high degree of cross-linking and low water absorption (Braden *et al.*, 1995).

2.2.3.2 Dimensional change (Figure 2.8)

Polymers swell in liquid, the degree of swelling depending on the chemical structure of the liquid. The higher the degree of swelling, the greater the loss of strength. High fluid sorption and solubility of lining materials may cause dimensional change, loss of compliance, discoloration, bad odour, and separation from the denture base. Solubility represents loss of components during immersion. The gradual leaching of plasticisers and residual monomers out of the denture soft lining material can also cause clinical problems. It is expected that the heat-curing soft acrylic materials would show less solubility than the self-curing ones due to less residual monomer. When immersed, the

plasticised soft acrylic lining materials undergo two processes; leaching out of plasticisers and other soluble materials, and absorption of water, saliva and other fluids (Wright, 1976; Braden and Wright, 1983). The balance between these two processes affects both the compliance and dimensional stability of the denture. When the material swells, stress builds between bonding surfaces or the viscoelastic properties of the denture soft lining materials change (Robinson and McCabe, 1982).

Figure 2.8 Soaking in a peroxide denture cleaner has resulted in surface bubbling and deterioration of a temporary denture soft lining material (tissue conditioner) (adapted from Braden, Wright and Parker, 1995).

2.2.3.3 Loss of adhesion (Figure 2.9)

Dentures constructed of two different materials can only be successful if a satisfactory bond exists between these two materials. The most common cause of failure of bonding is the basic chemical difference between the two materials (Storer, 1962; Mäkilä and Honka, 1979; Wright, 1984; Schmidt and Smith, 1983b; Wright *et al.*, 1985; Burns *et al.*, 1987). Complete separation does not always occur but local areas of separation between the liner and the base may become contaminated because of difficulty of cleaning between the two materials.

Figure 2.9 Local separation of a silicone rubber soft lining from the PMMA denture base (adapted from Braden, Wright and Parker, 1995).

2.2.3.4 Surface roughening (Figs 2.10-11)

Roughening of the denture soft lining material surface is common and is the most common reason given to replace the denture soft lining materials (Wright, 1984). The repeated sorption and desorption of water from the surface of the denture soft lining material may be one factor in producing the often reported roughening of the surface (Schmidt and Smith, 1983b; Wright, 1984, 1986; Braden *et al.*, 1995). Other factors which influence this are thought to be some of the constituents of foods and drinks, such as essential oils (Jepson *et al.*, 1993a) certain denture cleansers (Schmidt and Smith, 1983b; Wright, 1984) and the effect of surface contamination by *Candida albicans* (Mäkilä and Hopsu-Havu, 1977; Mäkilä and Honka, 1979; Braden *et al.*, 1995).

Figure 2.10 Roughening of the surface of a silicone rubber denture soft lining material in use (adapted from Braden, Wright and Parker, 1995).

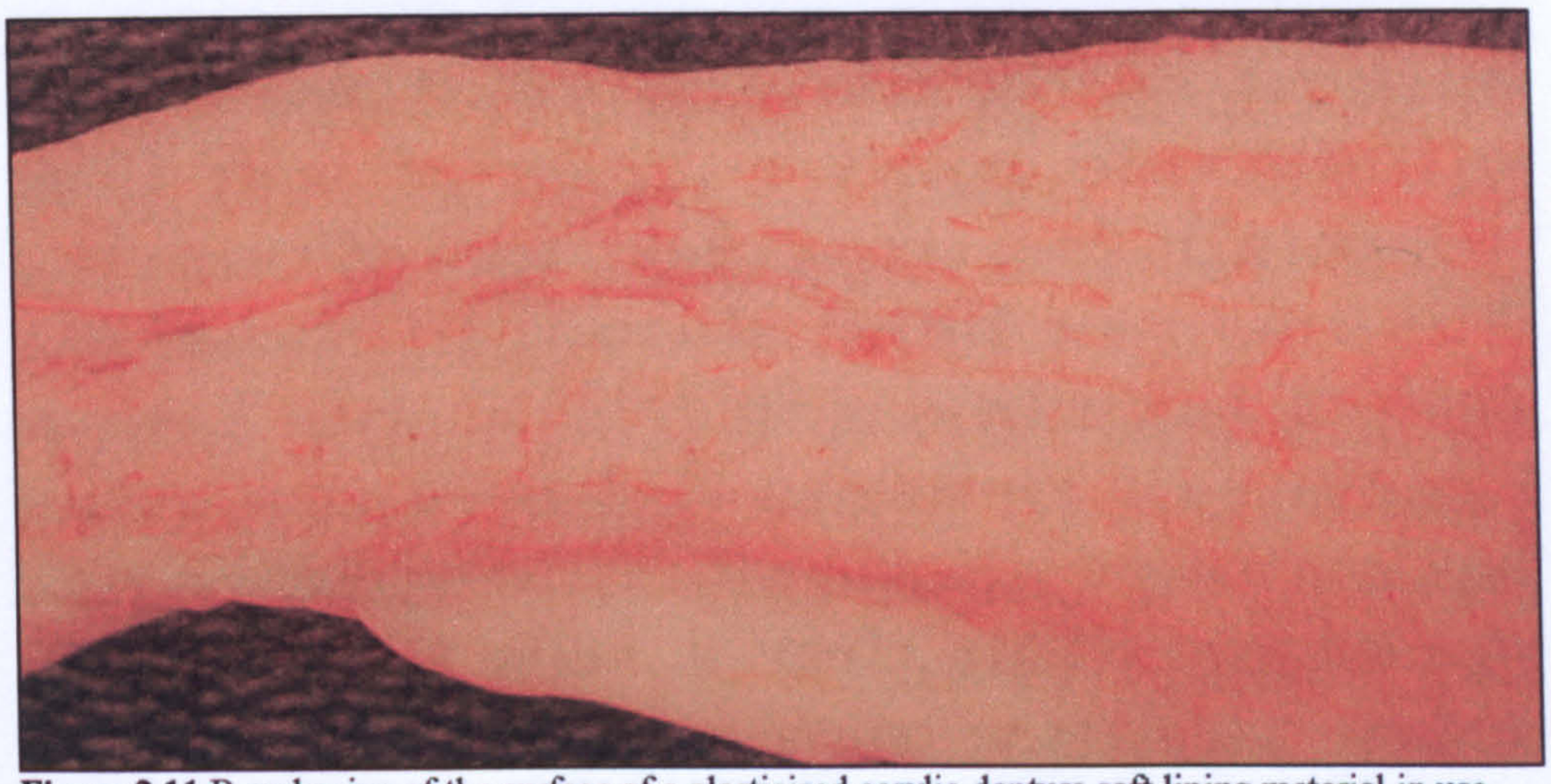


Figure 2.11 Roughening of the surface of a plasticised acrylic denture soft lining material in use (adapted from Braden, Wright and Parker, 1995).

2.2.3.5 *Candida albicans* colonisation (Figs 2.12-13)

Denture soft lining materials take up oral fluids. In the absence of an adequate regimen of denture hygiene, these fluids stagnate particularly in defects on the denture surface. This can cause the liner to become contaminated and foul. There are numerous reports of denture soft lining materials being colonized by *Candida albicans* under clinical conditions (Storer, 1962b; Mäkilä and Honka, 1979; Schmidt and Smith, 1983b; Wright, 1980b, 1986; Wright *et al.*, 1985; Burns *et al.*, 1987). The increased porosity of materials also can lead to plaque accumulation and *C. albicans* colonisation (Nikawa *et al.*, 1994). This colonisation provides a source for infections such as, denture stomatitis, oral, gastrointestinal and pneumopulmonary candidosis (Budtz-Jørgensen, 1990).

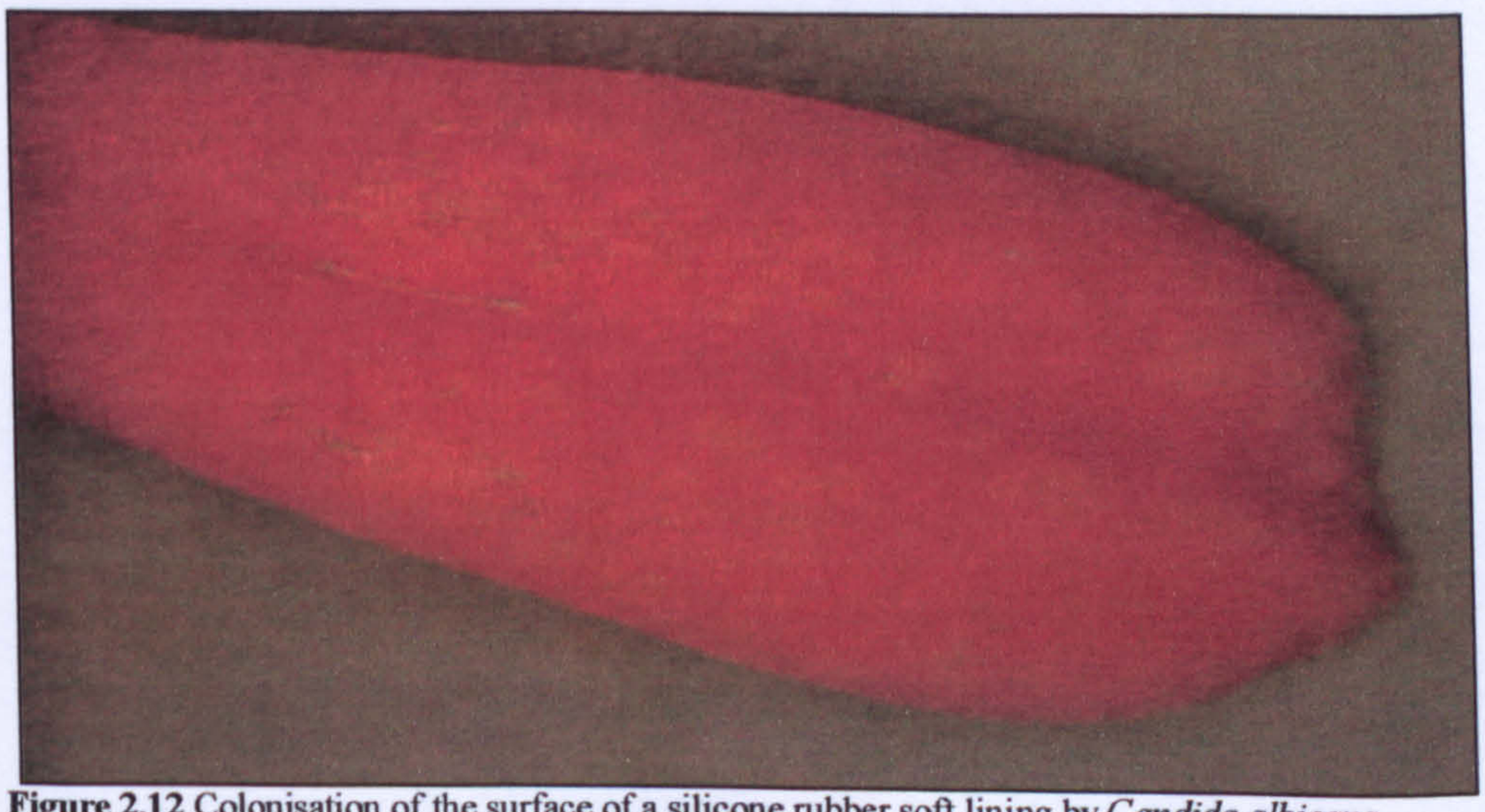


Figure 2.12 Colonisation of the surface of a silicone rubber soft lining by *Candida albicans* (adapted from Braden, Wright and Parker, 1995).

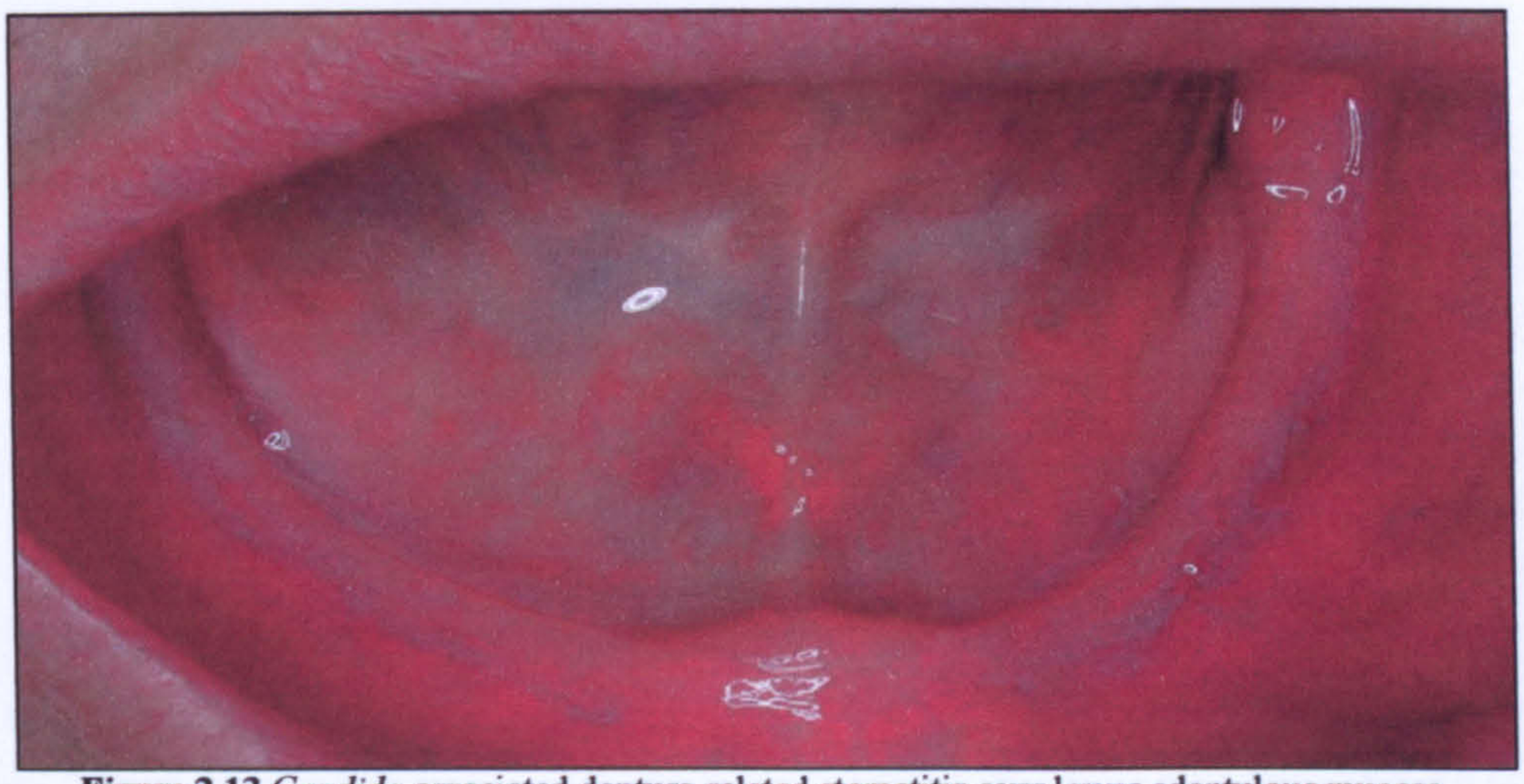


Figure 2.13 *Candida*-associated denture-related stomatitis over lower edentulous mucosa.

2.2.3.6 Poor rupture properties (Figure 2.14)

Rupture properties of denture soft lining materials may be characterised by their resistance to tearing. The energy necessary to tear an elastic material is related to the rate of deformation, the temperature of the test environment and the conditions of storage and use. In general, silicone rubbers and tissue conditioner-type materials are weaker than soft acrylic resin materials (Wright, 1981).

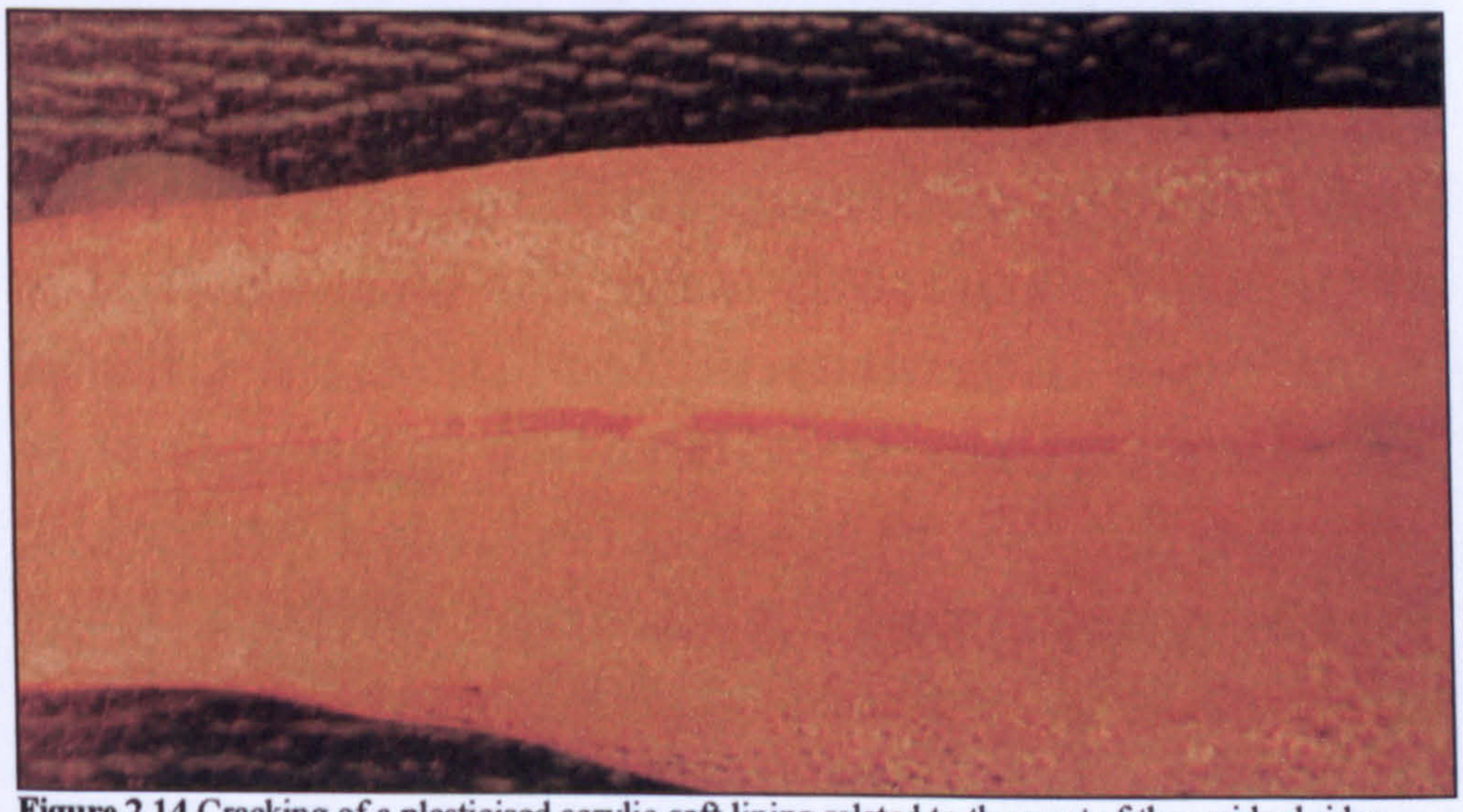


Figure 2.14 Cracking of a plasticised acrylic soft lining related to the crest of the residual ridge (adapted from Braden, Wright and Parker, 1995).

2.2.3.7 Summary

Denture soft lining materials have been available for many years because of continuing improvements of these materials. Failure of these materials has been attributed to

degradation of the materials, which leads to hardening, loss of adhesion between the methacrylate denture base and the denture soft lining material, yeast and microbial growth, dimensional change, and sorption of odours. The degraded materials may harm oral mucosa and result in the need for replacement with new material. This has a cost implication. Hence, investigation of the degradation of denture soft lining materials is an important clinical issue.

2.2.4 A brief history of denture soft lining materials

Most of today's denture bases are made with PMMA. However in the mid-1800s, dentures were made of vulcanised rubber. This cheap, easy-to-work material could be moulded to fit the mouth and made a good base to hold false teeth. It was fairly resilient but not overly aesthetic. Prior to these dentures were not truly dentures but rather false teeth being carved and fashioned out of wood and other materials such as ivory. Vulcanite dentures were very popular until the mid-1930s, when PMMA (pink plastic) denture bases replaced them.

2.2.4.1 Natural rubber

Denture soft lining materials have been used in dentistry for more than a century (Wright, 1984; Mack, 1989), with the earliest soft liner being natural rubber (*cis*-1,4-polyisoprene) (Twitchell, 1869) (Figure 2.15) In Twitchell's patent the material is described as: '*A soft rubber facing throughout all the portions of the plate which can come into contact to prevent the irritation that arises from the hard rubber pressing upon the gums and cheeks*'. No other soft liners are mentioned until 1940. However, the natural rubber material experienced a large water uptake which caused the material to swell and distort thus increasing the tendency for fouling (Lammie and Storer, 1958).

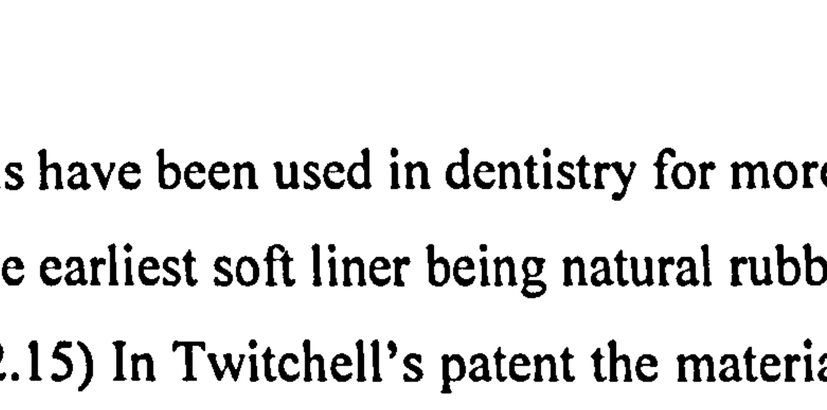


Figure 2.15 The structure of *cis*-1,4-polyisoprene

2.2.4.2 Vinyl copolymers

In 1945, Matthews used PVC (Figure 2.16) powder and a liquid di-butyl phthalate as a denture soft lining material. The plasticised PVC proved difficult to stabilise and was prone to leaching out of the plasticiser causing the material to harden and crack (Matthews, 1945; Lammie and Storer, 1958; Storer, 1962a; Wright, 1976). In 1958, Lammie and Storer reported their observation on the use of PVC, poly(vinyl acetate) (PVA) (Figure 2.16), and MMA copolymers. They found that PVC lost plasticiser (dibutyl phthalate). PVA had a high water absorption rate, accelerated plasticiser loss and stained easily. The use of plasticised PVC and PVA eventually diminished as new materials emerged.

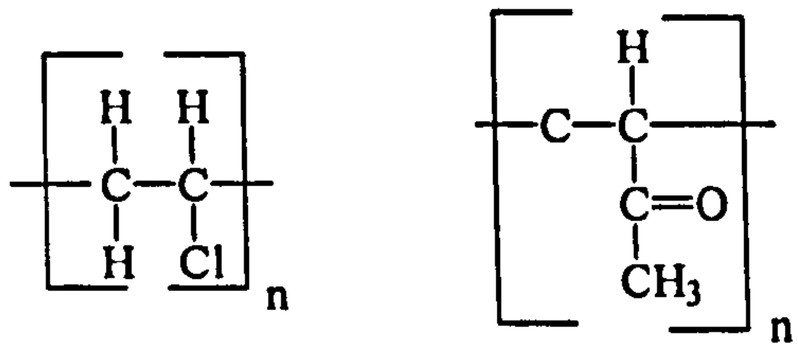


Figure 2.16 The structure of poly(vinyl chloride) (left) and poly(vinyl acetate) (right).

2.2.4.3 Acrylic-based compounds

The idea behind the plasticised methacrylate is that they were based on PMMA (Figure 2.17) (used in the denture base) plasticised with the addition of a di butyl or di octyl phathlate. These materials bond well to the PMMA denture (Wright, 1981) and initially fulfil the strength and softness criteria.

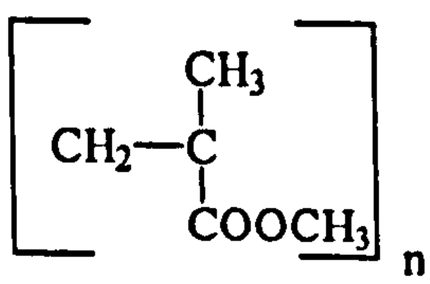


Figure 2.17 The structure of poly(methyl methacrylate)

The purpose of using plasticiser is to lower the T_g of normally hard materials, so that the modulus of the elasticity of the denture soft lining materials is reduced to a satisfactory level (McCabe, 1976). Immersion in water of plasticised methacrylate however leads to hardening due to the leaching out of the plasticiser (Wilson and Tomlin, 1969; Suchatlampong *et al.*, 1976; Wright, 1976). Improvements can be made by using PEMA and n butyl methacrylate, rather than PMMA, as the higher methacrylates are more

biocompatible, have lower exotherms and lower T_g (so less plasticiser may be used) (Riggs, 1997). Evaluating a higher molecular weight plasticiser, it proved virtually unextractable but the material failed clinically due to excessive water uptake which causing the formation of blisters within the material and mechanical failure (Parker and Braden, 1989).

2.2.4.4 Silicone-based compounds

Silicone rubbers were identified as a potential denture soft lining material from an early stage due to their low water uptake. Silicone rubbers based on PDMS (Figure 2.18) have been used as denture soft lining materials since 1958 (Lammie and Storer, 1958). This material solidifies by a cross-linking process (Figure 2.19). This cross-linking can be achieved either by heat, using benzoyl peroxide, or at room temperature, using ethyl silicate. Silicone rubber does not bond well to the PMMA denture base, so an adhesive (bonding agent) may need to be used. Silicone rubbers have several problems associated with their use, such as support of the growth of *Candida albicans*, porosity, poor tear strength, poor adhesion, and poor wettability by saliva.

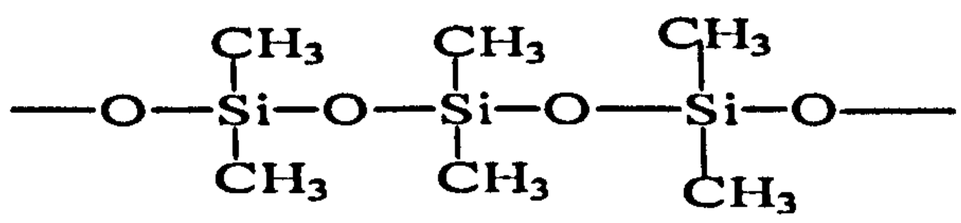


Figure 2.18 The structure of poly(dimethyl siloxane)

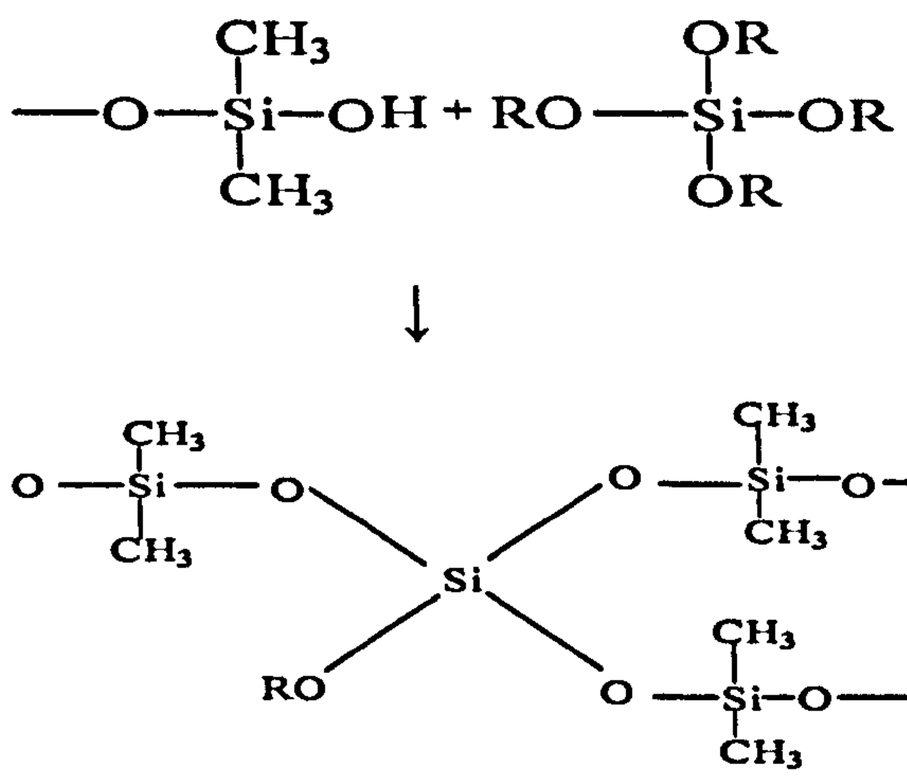


Figure 2.19 The crosslinking reaction of poly(dimethyl siloxane)

2.2.4.5 Other types of denture soft lining materials

Over the years the number and types of dental materials have proliferated, the newer materials have become more and more sophisticated.

Hydrophilic polymeric materials, such as hydroxyethyl methacrylate (Figure 2.20) polymerised with a small amount of cross-linking agent (e.g., EGDMA) (Braden *et al.*, 1997), seem at first to provide the ideal denture soft lining materials, hard enough to trim and adjust at room temperature yet maintaining a clinical softness at 37°C. However, the disadvantages of this material out weighed its advantages. These polymers when placed in water increase their original volume by over 37 per cent, thus the material has poor dimensional stability (Simpson, 1969).

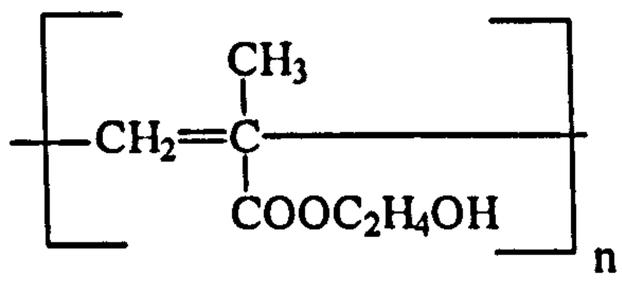


Figure 2.20 The structure of poly(hydroxyethyl methacrylate)

Polyphosphazine fluoroelastomers (Figure 2.21) including one famous commercial material, Novus™ manufactured by Hygienic Corporation, the base consisting of: poly (fluoroalkoxy) phosphazine elastomer and trimethylolpropane trimethacrylate monomer, crosslinked with EGDMA and initiated by the action of lauroyl peroxide (LP), has become available for use as a denture soft lining material. They are supplied in sheet form and are manipulated in a similar manner to the heat cured silicone rubber products. Von Fraunhofer and Sichina (1994) demonstrated Novus™ to have a greater tear strength and to be more compressible than Molloplast-B®, a silicone elastomer, but some researchers have reported Novus™ to have high water uptake in comparison with Molloplast-B® silicone rubber (Kawano *et al.*, 1994b, Braden *et al.*, 1995). These materials have been withdrawn from the market due to lack of availability of the elastomer.

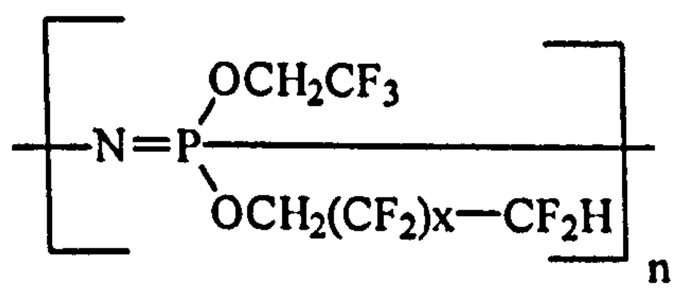


Figure 2.21 The structure of polyphosphazine Fluoroelastomer

There have been several light-cured denture soft lining materials including Triad Resiline™ from Dentsply based on urethane dimethacrylate. This material requires special moulds as with the light-cured denture base materials. It does not bond well to the denture base. The newest addition is Clearfit LC™ from Kuraray, Japan based on polyisoprene, which has not been reported in the literature.

2.2.4.6 Novel alternative methacrylate/ elastomer blends

The combination of a methacrylate monomer with an elastomer may result in a material exhibiting advantages of both polymers i.e. good adhesion to PMMA denture and high mechanical strength. Braden *et al.* (1997) consider it to be essentially a soft acrylic material with no leachable plasticiser. Many elastomers are considered to be compatible with methacrylate monomers (Parker and Braden, 1990)

Blends of butyl elastomer/ n-butyl methacrylate (nBMA) were first developed as a result of studies undertaken by Parker and Braden in 1996. They initially dissolved natural rubber in methacrylate monomers containing an appropriate initiator and crosslinking agent. These materials exhibited high mechanical strength and good adhesion to the denture base, with adhesion values between those of established acrylic and silicone denture soft lining materials, but the water soluble impurities in natural rubber lead to this material's unfavourably high water uptake. However, Riggs *et al.* (2002) have reported bromo butyl elastomer to have low water uptake in comparison with butyl and chlorobutyl elastomer for use in formulations.

2.2.5 Classification of denture soft lining materials

2.2.5.1 Long-term denture soft lining materials

2.2.5.1.1 Soft acrylic resin based materials

Acrylic resin (heat and autopolymerised) denture soft lining materials are usually supplied as powder/ liquid systems, the composition of which varies from one product to another.

2.2.5.1.1.1 Heat polymerised soft acrylic resin

Heat polymerised soft acrylics are based on a polymer powder–monomer liquid system, very similar to PMMA denture base. The polymer powder is usually PEMA or butyl/ethyl methacrylate copolymer. The monomer liquid can be a range of higher methacrylate, such as n-butyl, ethyl or 2-ethoxyethyl methacrylate and also contain a plasticiser, such as butyl phthalyl butyl glycollate (BPBG), di-n-butyl phthalate (DNBP) or acetyl tributyl citrate (ATBC) (Wright, 1981; Braden *et al.*, 1997). An example of commercial brand is Vertex™Soft. The powder is PEMA, and the liquid comprises of higher methacrylates and ATBC as a plasticiser.

When the powder is mixed with the monomer, the plasticiser in the liquid swells the powder particles to form a dough which may then be processed. The initiator is generally residual BP which is present in the polymer powder as part of the manufacturing process of the methacrylate polymer. The dough can then be moulded, packed, processed and cured by heat as a result of the residual peroxide free radical polymerisation. A large amount of plasticiser is added to reduce the glass transition temperature of the polymer so that it remains soft below mouth temperature.

It requires no adhesive to form a bond between denture and lining material. This material is also reasonably resistant to fungal growth. Unfortunately, this type of material is well known for its gradual hardening in the mouth due to loss of plasticiser.

2.2.5.1.1.2 Autopolymerised soft acrylic resin

The formulations of autopolymerised soft acrylics are very similar to the heat-polymerised types except they contain an activator, an aromatic amine (e.g., N, N-dimethyl-p-toluidene), in the monomer liquid (Braden *et al.*, 1997). The advantage is that they polymerise at room temperature, thus, offer more convenience. However, this may result in a higher level of free monomer remaining in the material, as this method of polymerisation is not as efficient as heat-polymerisation, and will result in reduced mechanical and biocompatibility properties (Wright, 1981).

Hence, methyl-methacrylate-free denture soft lining materials are on the market to avoid the risk of sensitivity problems. One example of a commercial brand is EverSoft®. EverSoft® claims not only to be a long-term denture soft lining material, but also to be methyl 'methacrylate free'. This material is similar to a tissue conditioner formulation, which is provided as a two-phase component like the plasticised acrylics. The powder is PEMA, and the liquid is comprised of plasticiser, such as dibutyl phthalate, ethyl acetate and ethyl alcohol. Chemically EverSoft® is more like a tissue conditioner than a long-term denture soft lining materials. Generally, EverSoft® requires some heat to facilitate the gelation process. It is easy to use. The powder and liquid are mixed to appropriate viscosity, placed onto the clean roughened denture tissue surface and then into the mouth until it has set. After this, it is removed from the mouth, cured in hot water for only 15 minutes, trimmed, sealed, and delivered to the patient. According to the EverSoft®'s manufacturer, the sealer based on methyl ethyl ketone forms a non-absorbent, high gloss exterior surface that repels fluids, bacteria, and odour while it maintains the softness (MSDS for EverSoft®, 2004). The manufacturer also claimed EverSoft® has excellent material properties, such as bonding to the denture chemically without intermediate bonding agent, retaining long-term compliance and biocompatibility. This material still needs to be fully investigated.

Generally, heat-polymerisation is more efficient than autopolymerisation as the latter has higher levels of free monomer remaining in the materials. The presence of the free monomer can result in lower mechanical properties and reduce biocompatibility. The only advantage of autopolymerised type over the heat-polymerised is convenience.

2.2.5.1.2 Silicone based materials

Silicone rubbers can also, like acrylics, be heat polymerised or autopolymerised (room temperature cured). Silicone rubber is generally produced from a range of PDMS. These are normally viscous liquids which, on cross-linking can provide high molecular weight compositions with different level of elasticity. Plasticisers are not requiring as their glass transition temperature is well below room temperature. The cross-linking agent is

normally an alkyl silicate and the reaction may be catalysed by an organic-metal salt such as tin-octoate (McCabe, 1976).

2.2.5.1.2.1 Heat polymerised silicone rubbers

Heat-polymerised silicones are generally one-component systems supplied as a paste or rope form. They can be based on α-ω-dihydroxy terminated PDMS. Cross-linking is achieved by the presence of BP and the application of heat. Additionally acryloxyalkyl silane improves the cross-linking of the silicone rubber (Wright, 1981) One famous example of commercial brand is Molloplast-B®.

Molloplast-B® is supplied as a one-paste system activated by heat (boiling water for 2 hours) or by use of a microwave oven. Wright (1981) states that because silicone rubbers have no natural adhesion to PMMA, an adhesive, γ-methacryloxypropyl trimethoxysilane, composed of a silicone polymer in a volatile solvent is essential (Figure 2.22). The main advantage of this material is its low water uptake, but there are a number of problems associated with Molloplast-B® silicone liner. The most common failure is the failure of adhesion between the soft lining and the denture base. Roughening of the surface of Molloplast-B® silicone liner was the second most common reason given for the need to replace the Molloplast-B® soft lining. Thirdly, fungal growth on Molloplast-B® silicone denture soft lining materials was common, the most common being *Candida albicans* (Wright, 1984). However, reports of success rates from 83% to 68% over six to nine years have been noted (Schmidt and Smith, 1983ab; Wright, 1994). A clinical case even shows one Molloplast-B® soft lined mandibular denture which was worn for over ten years before tooth wear necessitated the replacement of denture (Braden *et al.*, 1995).

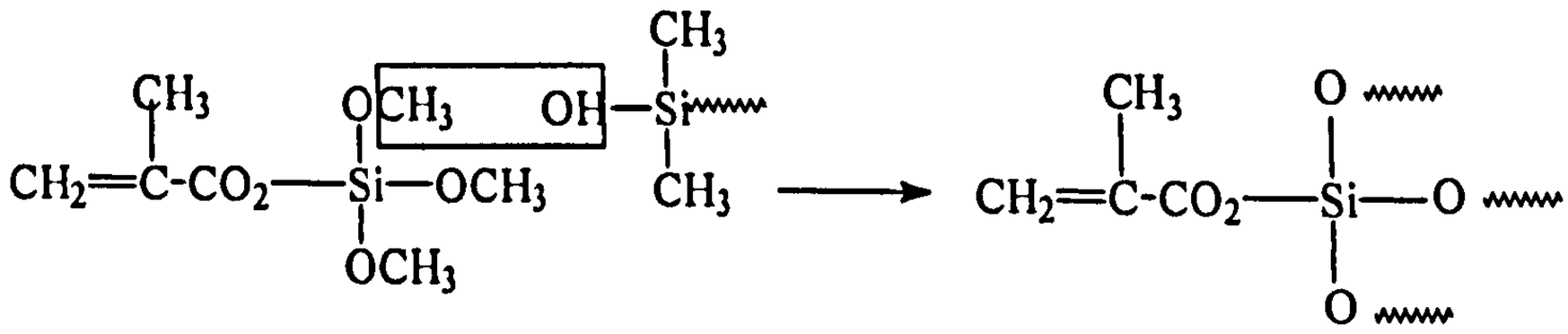


Figure 2.22 The chemical reaction of a α-ω-dihydroxy terminated poly(dimethyl siloxane) with γ-methacryloxypropyl trimethoxysilane.

2.2.5.1.2.2 Autopolymerised silicone rubbers

Most room temperature cured silicone elastomers are similar to the condensation silicones used as dental impression materials. Their basic polymer is based on α-ω-dihydroxy end blocked PDMS but differ in the cross-linking agent and catalyst used and in the percentage of filler. These differences are reflected in the water absorption characteristics and in the effect on the growth of *Candida albicans* (Wright, 1981). One example of a commercial brand is Mollosil®.

Wright (1981) concluded in his investigations that room temperature polymerised condensation silicone rubbers have several disadvantages, such as the high level of water absorption leading to poor dimensional stability, poor rupture properties, poor wettability, and the presence in the cross-linked material of a chemical which may act as a primary irritant in the mouth.

A new type of silicone denture soft lining material is based on chemistry similar to that used in polyvinylsiloxane impression materials. In contrast with the condensation silicones, the addition reaction polymer is terminated with vinyl polysiloxanes and is cross-linked with vinyl groups activated by a platinum salt catalyst. Both base and catalyst pastes contain a form of the vinyl silicone, which can be supplied in cartridges similar to the impression materials. Paste one is composed of vinyl terminated siloxane platinum based catalyst filler. Paste two is composed of vinyl terminated siloxane hydrogen terminated siloxane filler. Curing occurs by an addition reaction involving the end groups in the presence of platinum-based catalyst (usually chloroplatinic acid) (Anusavice, 1996). An example of commercial brand is Ufi Gel SC. According to the manufacturer's technical data sheet, Ufi Gel SC is easy to use and can be applied using the cartridge system by automixer and dispenser. With these mechanical devices, there is greater uniformity in proportioning and in mixing, and fewer air bubbles are incorporated into the mix. The manufacturer's technical data sheet also claimed Ufi Gel SC has excellent material properties, such as long term elasticity and biocompatibility. This new addition type silicone still needs to be fully investigated.

2.2.5.2 Short-term denture soft lining materials (tissue conditioners)

Tissue conditioners remain soft for a limited period (a few days to weeks) and can be used when it is necessary to give the oral mucosa time to recover from inflammation due to ill-fitting dentures or after surgery. They also can be used in the treatment of denture related stomatitis and as a functional impression material. They usually consist of a two-component powder and liquid system. The powder is composed of PEMA or a related copolymer (butyl/ethyl methacrylate copolymer) while the liquid is usually a mixture of ethyl alcohol as a solvent and dibutyl phthalate as plasticiser. Usually, the gel is initially softer with a high concentration of volatile solvent. However, leaching and evaporation of these components lead to rapid hardening of the material in the mouth (Qudah *et al.*, 1990). One famous example of a commercial brand is Viscogel™ manufactured by Dentsply.

2.2.5.3 Experimental denture soft lining materials

The basic philosophy behind elastomer/methacrylate hybrid is to incorporate a polymer with a low glass transition (elastomer) into a methacrylate system, thus creating a denture soft lining material with all the advantages of the current methacrylate-based materials without the need for plasticisation (Parker *et al.*, 1996).

2.2.5.3.1 Butyl rubbers

Butyl rubbers are amorphous, non-polar synthetic elastomers which are vinyl polymers. They are homopolymers of isobutylene and consist of a regular carbon-hydrogen backbone with unsaturation present at the chain ends. It is characterised as an extruded plastomer, which is a material that processes like a thermoplastic but has properties of a rubber. The molecular structure of polyisobutylene (PIB) leads to a variety of properties (Gent, 2001) including:

- Excellent weathering and aging stability
- Excellent moisture resistance
- Good resistance to ozone, chemical and UV light
- Low gas permeability
- High elasticity and flexibility at low temperatures

2.2.5.3.2 Chemistry of butyl rubbers

PIB is very similar to polyethylene and polypropylene in structure, except that every other carbon is substituted with two methyl groups. It is made from the monomer isobutylene, by cationic vinyl polymerisation. This involves the use of an initiator or cation which attracts a pair of electrons from the carbon-carbon double bond and forms a single bond with the initiator. In turn this causes one of the carbon atoms to become more positively charged enabling it to readily react with another monomer molecule. The process is repeated and isobutylene co-isoprene rubber (IIR) is formed (Figure 2.23).

PIB has no double bonds so it cannot be vulcanised or hydrogenated. This is overcome by incorporating 1% (3% maximum) of isoprene to copolymerise the isobutylene. The chemical formulation of butyl rubber is poly (isobutylene-coisoprene). The butyl rubber is typically crosslinked by using sulphur but there are two other alternative methods to achieve crosslinking. The first method involves the reaction of butyl gum with phenol formaldehyde resin. The other crosslinking reaction involves the reaction of the gum with p-quinone dioxime dibenzoate and lead oxide. The ultimate properties of the rubber are as a result of varying the unsaturation and molecular weight of the base polymer and the branching of the gum stock (Botros and Abdel-Nour, 1997).

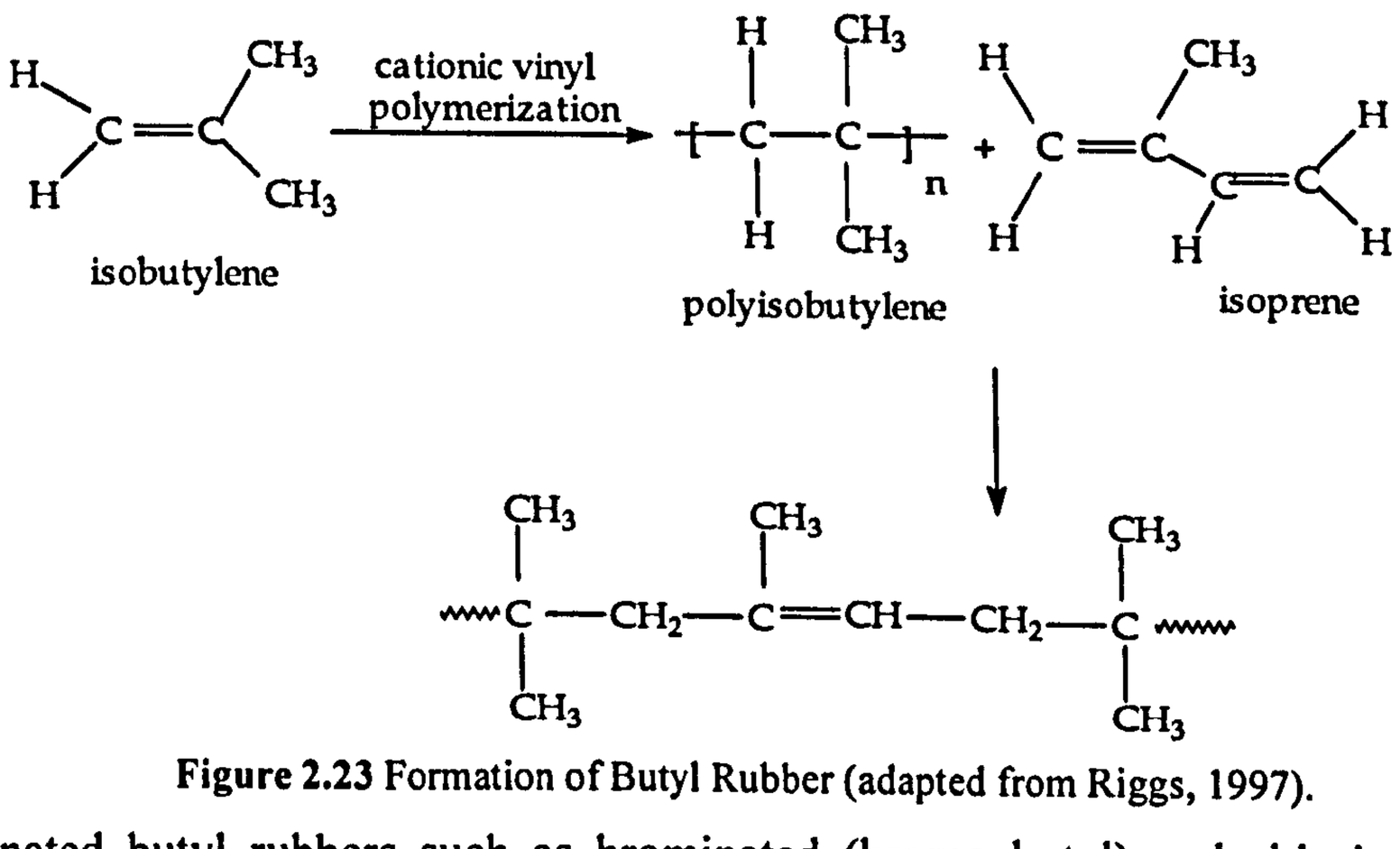


Figure 2.23 Formation of Butyl Rubber (adapted from Riggs, 1997).

Halogenated butyl rubbers such as brominated (bromo butyl) and chlorinated (chloro butyl) were an expansion of butyl rubber developed in the 1950's and 60's. Halogenated butyl rubbers are more reactive than standard butyl rubbers which lead to them having

higher vulcanisation rates, and are also more able to be co-vulcanised with other rubbers including highly unsaturated elastomers. These properties permitted the production of tubeless tyres, and make brominated and chlorinated butyl rubbers the polymers of choice in the tyre industry. Bromo butyl is faster curing than chloro butyl and has better adhesion to rubbers with high unsaturation.

2.2.5.3.3 Chemistry of *n*-butyl methacrylate (*n*BMA)

Acrylic monomers like *n*-butyl methacrylate (*n*BMA) (Figure 2.24) are colourless liquids that contain a small amount of inhibitor like hydroquinone (0.006% w/w) and are stored in dark brown glass bottles as they may polymerise under the action of UV light (Anderson, 1976). The structure of nBMA typically has a methacrylate backbone and butyl group (C_4) on the side chain.

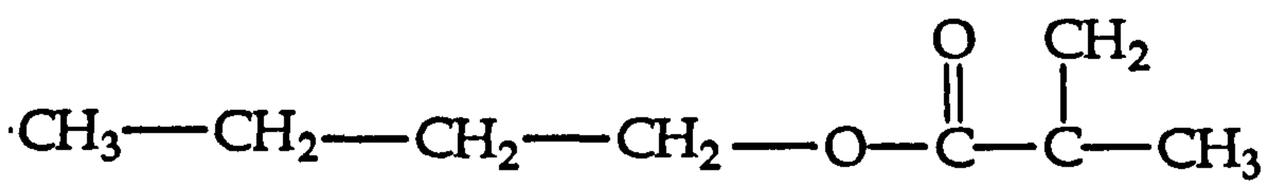


Figure 2.24 The structure of poly (n-butyl methacrylate).

2.2.5.3.4 Crosslinking agents

Crosslinking agents in copolymers serve to initiate formation of an insoluble three dimensional crosslinked network during the process of polymerisation. The crosslinking agents help to anchor and restrict the motion of the polymer chains within the network.

Deb *et al.* (1997) investigated the effect of 2, 5 and 10% of each of the following agents: EGDMA (Figure 2.25), triethylene glycol dimethacrylate (TEGDMA) and polyethylene glycol dimethacrylate (PEGDMA) on the effect of crosslinking agents on acrylic bone cements based on PMMA and the 2% EGDMA proved to be the most effective in enhancing the tensile strength of bone cement.

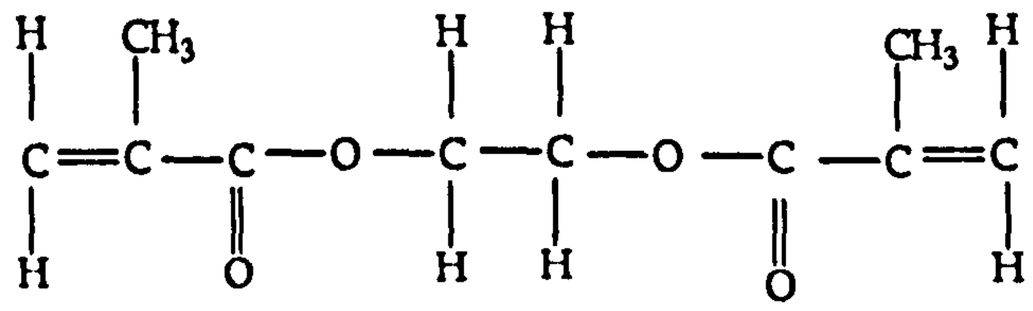


Figure 2.25 The structure of ethlylene glycol dimethacrylate (EGDMA).

The addition of crosslinking agent in denture soft lining materials has both advantages and disadvantages. The advantages are it will enhance tensile strength and solvent resistance. However, excessive levels of crosslinking agent will increase the effect of binding polymer together and reduce flexibility of denture soft lining materials.

2.2.5.3.5 Initiators

An initiator like BP ($C_{14}H_{10}O_4$) or LP ($C_{24}H_{46}O_4$) (Figure 2.26) was used to initiate the polymerisation and overcome the effect of the inhibitor in the n-butyl methacrylate monomer. The peroxide forms two radicals, one which reacts with the monomer and the other with the elastomer component to cause grafting of the copolymer (Riggs, 1997). Alternatively action of the radical may result in only polymerisation of some monomer and crosslinking of elastomer chains. Grafting does depend on the saturation of the elastomer chains, unsaturated chains result in more monomer grafting during initiation. The lauric acid produced as a by-product is insoluble at 37°C making it a more favourable for use than BP that forms benzoic acid which is soluble at 37°C thus is more prone to leaching from the material (Riggs, 1997).

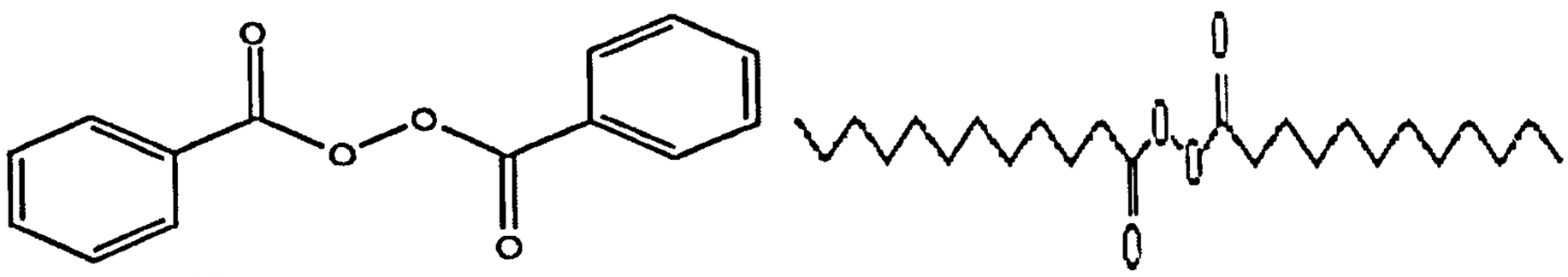


Figure 2.26 The structure of benzoyl peroxide (left) and lauoryl peroxide (right).

Investigations previously undertaken (Riggs, 1997) researched the use of butyl elastomers with various monomers to identify an optimum formulation as a potential denture soft lining material. The material with the most promising properties was the butyl elastomer/ butyl methacrylate system.

2.3 Physical properties of denture soft lining materials

2.3.1 Water absorption characteristics

Water sorption of the dental materials is of importance clinically, particularly in relation to the dimensional stability and durability of the material. When materials are placed in

an aqueous environment, their dimensional and structural integrity may be affected because they absorb water by a process of diffusion (Braden and Wright, 1983). Constituents also may be lost by a diffusion process. This may have serious consequences especially if these results in a change in the material properties incorporated to its intended function, or the biocompatibility could become compromised if these components are toxic or irritant (Braden and Causton, 1971; Parker *et al.*, 1997). As well as the potential for soluble material being leached with possible toxic effects, excessive water uptake can cause distortion and allow ingress of micro-organisms. It is desirable that the levels of uptake and loss be as small as possible.

As denture soft lining materials are used in the oral cavity, the knowledge of their behaviour in the moist environment is a key to evaluating their performance. So, *in vitro* water absorption characteristics are an important property to evaluate and can give an indication as to the behaviour of material *in vivo*. Unfortunately, it should be noted that denture soft lining materials are rarely placed in "pure" water in the oral cavity, but rather bathed in saliva, food and drinks, or soaked in denture cleansers overnight. These fluids are far more complex, containing a variety of organic and inorganic components which may influence the manner in which fluid is absorbed into the materials.

2.3.1.1 Mechanism of water absorption

There are a variety of ways in which water is taken up by a polymer, these mechanisms can act independently of one another or it is possible for more than one process to be at work at any given time (Kalachandra and Kusy, 1991). The introduction of a mathematical model from a series of papers by Muniandy and Thomas (1984; 1988) provided a better scope in understanding the water uptake of elastomers. They assumed the presence of water soluble components in the polymer resulted in high water uptake. Parker and Braden (1989) applied the mechanism following the work of Muniandy and Thomas (1984) to denture soft lining materials. They proposed that water uptake is governed by water soluble components within the polymer matrix, which gives rise to a chemical potential gradient (Parker *et al.*, 1997). As water diffuses into the material reaching sites of impurity, as shown in the Figure 2.27, a solution droplet is formed.

The solution droplet has an osmotic potential depending on the size and type of impurity in the droplet. This gives rise to an osmotic pressure gradient between the solution droplet and external solution in which the material is immersed. As a result, water diffuses into the material, and these droplets continue to grow in size and consequently deform the material surrounding them. The deformation of the material around the droplet results in a restraining force which opposes the deformation exerted on the material by the droplet. Equilibrium water uptake is reached when the osmotic pressure difference is equal to the restraining force. Uptake should therefore be lower from solutions of higher osmotic pressure (Parker *et al.*, 1997, 1999). A reduced water uptake in artificial saliva has been noted by other studies (Kazanji and Watkinson, 1988a); however, they did not offer any theory to explain this phenomenon.

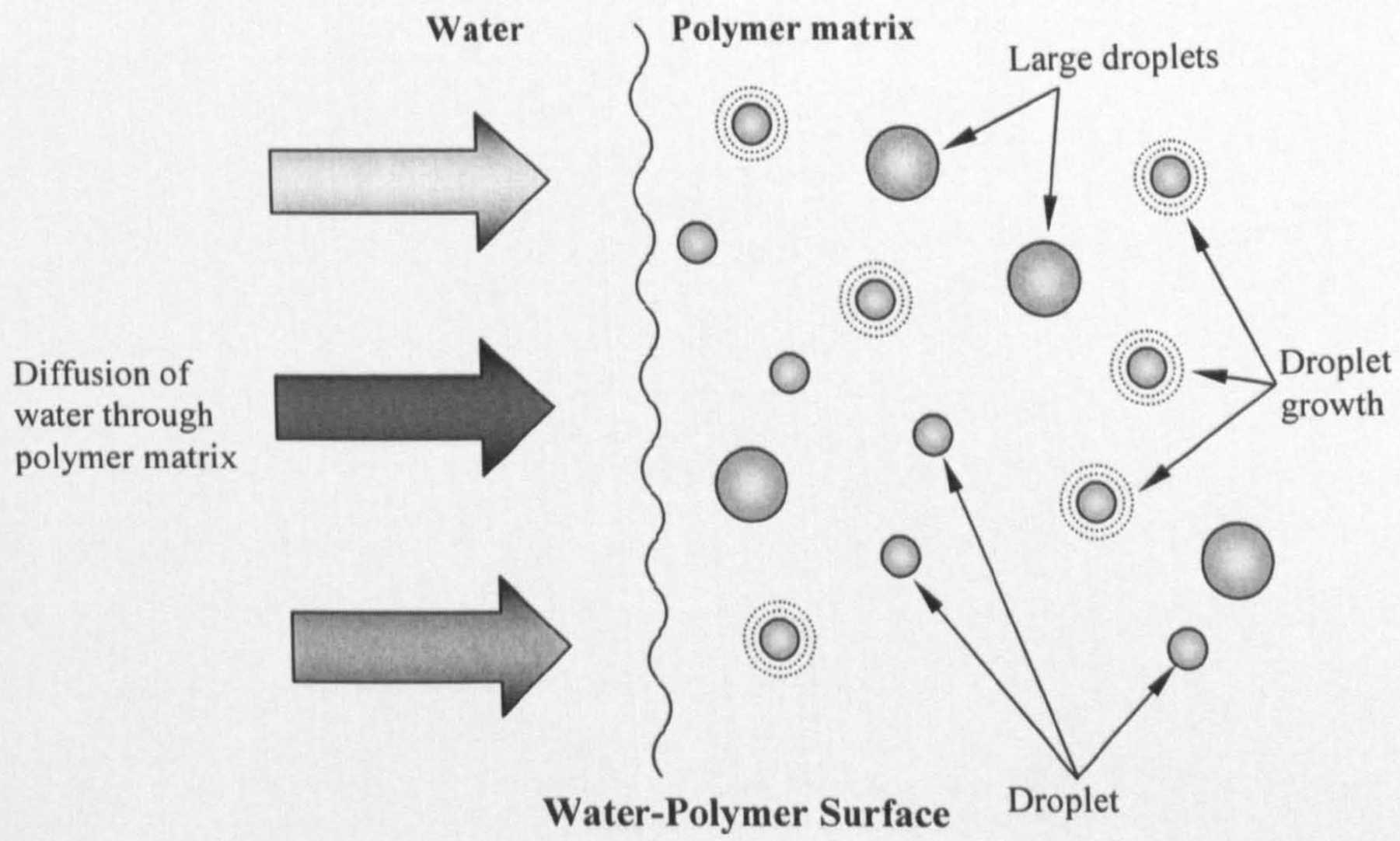


Figure 2.27 Representation of water uptake mechanism (adapted from Braden *et al.*, 1997).

Water uptake is also dependent upon the mechanical properties of the material. The material may creep around the droplet whilst growing under a constant stress. The action of creep would relax the restraining force and extend the absorption process. The material will absorb a greater amount of water depending on the particular creep characteristics of the material (Riggs, 1997). An additional theory suggests that the uptake is via polar attraction (Fedors, 1980). Clusters of water, which behave like pseudo-droplets, are formed when water is attracted to the groups (Patel and Braden, 1991).

2.3.1.2 Water uptake of denture soft lining materials in distilled water, artificial saliva and other solutions

In 1960, Travaglini *et al.* were the first to report the weight changes of denture soft lining materials in water. Specimens (48 by 48 by 2 mm), from ten early denture soft lining materials, were stored in distilled water at 25°C for 30 weeks. The surface of the specimens after 30 weeks was rough and had a blanched appearance on visual observation. Travaglini *et al.* speculated that the visual observations and the weight changes for the acrylic resin (from -1.6 to 3.5 per cent) and vinyl resin materials (2.0 per cent) were due to water sorption and leaching out of plasticisers. The weight increases (3.4 per cent) of silicone rubber materials were attributed to the absorption of water by fillers used in the materials. However, the details of the results were not shown clearly by graph or table. Further the temperature of 25°C did not simulate oral conditions (37°C).

One year later, Craig and Gibbons (1961) reported further results of the weight changes of denture soft lining materials in distilled water. Specimens (48 by 48 by 2 mm), from same ten early denture soft lining materials, again were stored in distilled water at 25±1°C for 12 weeks, and developed rough and grainy surfaces. Craig and Gibbons repeated the speculation that the visual observations and the weight changes for the acrylic resin (from -0.9 to 3.8 per cent) and vinyl resin materials (2.2 per cent) were due to water sorption and leaching out of plasticisers, and the weight increases (4.3 per cent) of silicone rubber materials were attributed to the absorption of water by fillers used in the materials.

In 1962, Eick *et al.* (1962) reported the weight changes of 9 early denture soft lining materials stored in water at 37°C on the basis that this temperature simulated oral conditions. They repeated the previous work of Travaglini *et al.* (1960) but the specimens were immersed at 37°C and they increased the storage time to six months. The weight increases from 1.1 to 3.7 per cent after one month in water at 37°C were a little larger than at 25°C. However, the weight increases after six months in water at 37°C varied from 2.0 to 22.1%. These results showed the materials had not reached equilibrium in the test periods and the test periods were too short for the expected life of the materials.

In the same year, Storer (1962) reported his work on different types of denture soft lining materials which included natural rubbers, plasticised polyvinyl resins, methacrylate copolymers and silicone rubbers. The denture soft lining materials were immersed in water at 37°C for up to 30 months and the weight changes and the percentage volume changes calculated. Storer speculated that a final negative volume change for plasticised materials was due to the loss of soluble materials which sometimes exceeded water absorption. The non-plasticised materials showed little increase in volume and the water absorption of silicone rubbers varied possibly dependent on the nature of the filler. However, no attempt was made to identify the fillers involved.

Three years later, Bates and Smith (1965) published their work on a more extensive list of materials which were divided into heat-cured and cold-cured acrylic resin type, heat-cured and cold-cured silicone rubber type and polyvinyl chloride-acetate type. Molloplast-B® (a heat-cured silicone rubber type) was first examined in an *in vitro* study. Specimens were immersed in water, olive oil and peppermint oil at 37°C for 30 days and then dried to a constant weight over phosphorus pentoxide. By measuring the weight changes between the fluid immersion period and the final dehydrated constant weight, Bates and Smith were able to quantify the actual amount of water absorption over this period. Bates and Smith recognised that large water absorption may lead to swelling and stresses at the denture base/ soft lining interface which could promote dimensional instability and reduce the bonding between the denture soft lining material and acrylic base material. Ideally, the water absorption should be similar to that of the acrylic resin base material which was reported as 2.2%. Bates and Smith recommended Molloplast-B®, suggesting that if treated correctly in the laboratory and by the patient, it will survive wear for three or more years although the water absorption value of Molloplast-B® was 3.8%, larger than 2.2% in acrylic resin. However, the test period was too short to confirm the proposed clinical success. It should be noted that Bates and Smith found considerably different behaviour for the two types of oil. Olive oil tended to extract plasticiser and little swelling was observed (% weight change from -12.2 to 0.6 per cent; Molloplast-B® was -3.1 per cent). Peppermint oil was rapidly absorbed and there was considerable swelling (% weight increase from 24 to 380 per cent; Molloplast-B® was 45 per cent).

The silicone-based materials showed the best all-round resistance, but the self-curing acrylic materials were less satisfactory. This report was important in relation to resistance to fatty foods and other sources of essential oils. Unfortunately, there was no further report subsequently.

Ellis *et al.* (1977) were first to report the different fluid sorption behaviour of a methacrylate-based denture soft lining material (Coe-Soft) when immersed in distilled water or artificial saliva. Freshly processed specimens, one mm in thickness, were immersed in distilled water or in artificial saliva (KSCN, 0.22 gms; $NaHCO_3$, 0.77 gms; NaCl, 0.23 gms; $CO(NH_2)_2$, 0.13 gms; K_2HPO_4, 9.95 gms; $CaCl_2$, 0.16 gms; made up to 1 litre with distilled water) at 37°C for 100 days. Initially there was a decrease in weight recorded in all specimens because the diffusion out of ethanol was faster than fluid absorption. Subsequently the behaviour of specimens in each case differed. In distilled water the specimen showed a continuous weight increase by absorbing water for up to 100 days with no signs of equilibrium being reached. In contrast, in artificial saliva, following the initial decrease in weight, the weight increased slightly and then continued to decrease again with weight loss for up to 100 days. Although no explanation of the differences was proposed, the authors clearly stated that sorption studies in pure water were inadequate when assessing the clinical performance. Moreover, the period of study was still too short to represent normal clinical use.

In 1977, Louka *et al.* reported two different methods for improving the wettability of denture soft lining materials. The two methods were: (1) a paint-on technique for depositing a thin film of silicon tetrachloride on the surface, (2) a modification of a vacuum discharge treatment by CASING (cross-linking by activated species of inert gases). Four denture soft lining materials (heat-cured acrylic Palasiv™, Cold-cured acrylic Soft Oryl™ and Flexacryl-Soft™, Heat-cured silicone Molloplast-B®, and Cold-cured silicone Mollosil®) were used. Incidentally, they investigated the water sorption by weight change. Specimens were fabricated in the form of circular disk 50 mm in diameter and 4 mm thick. One-half of the thickness consisted of auto-polymerised denture base acrylic and the remaining half consisted of the denture soft lining material. Specimens

were immersed in distilled water at 37±1°C for up to 4 weeks. The weight changes of the silicone tetrachloride-treated group and the CASING group were 20 mg and 5 mg, respectively. They stated that the silicone tetrachloride-treated surface rendered the polymer surface hydrophilic leading to high water sorption, and that the CASING-hydroxy treatment depended on the polar changes of the polymer surface group leading to less water sorption. However, the explanation of water sorption was complicated because the specimens combined autopolymerising denture resin, denture soft lining material and surface treatment. Thus the results may be related to a combination of factors each of which could not be isolated.

Two years later, Ellis *et al.* (1979) reported the water immersion characteristics of Coe-Soft over a period of 131 days. Water diffused into Coe-Soft without limit throughout the period of experiment, with a weight increase which was approximately linear with respect to time^{½} (minutes^{½}). The authors stated that the composition of Coe-Soft changed continuously during use and recommended the use of one mm thick specimens for studies of changes in mechanical properties because of similar thickness being used in the mouth. Unfortunately, the authors did not discuss the water absorption behaviour of Coe-Soft in artificial saliva where possibly the conditions would be more complex.

In 1983, Braden and Wright reported the absorption and desorption of denture soft lining materials in distilled water. Specimens, flat thin strips, were immersed in distilled water at 37±1°C for over five years. The detail of the specimen dimension was not reported thus making comparisons with other studies difficult. When equilibrium was reached, or, when equilibrium was not reached, after an extended period of absorption measurements, the material was transferred to a oven at 37±2°C containing a desiccant, and weighting was continued at appropriate intervals. Ideally, further absorption and desorption cycles should be carried out until all the soluble material has been extracted. However, this ideal situation had not been reached for most materials (except two silicone rubber materials: Per-Fit and Molloplast-B®). Braden and Wright stated clearly that the period of immersion in water for the first absorption cycle should be as long as possible because most of the experimental materials did not reach the equilibrium state within five years.

Hence, a prolonged absorption period is essential to calculate the relative influence of water absorption and loss of soluble material over a clinically relevant period.

Five years later, Kazanji and Watkinson (1988a) reported the water absorption and solubility of denture soft lining materials in artificial saliva and distilled water. This was the second paper to investigate the fluid absorption behaviour in artificial saliva although the formulation was different from Ellis *et al.* (1977). Moreover, Kazanji and Watkinson not only investigated methacrylate-based denture soft lining materials (heat-cured Softic-49 and Coe-Super-Soft, cold cured Coe Soft) but also examined silicone-based denture soft lining materials (heat-cured Molloplast-B®, cold-cured Flexibase). Specimens, 45 mm in diameter by 1 mm in thickness, were immersed in distilled water or artificial saliva (ammonium chloride, 0.233 g/L; calcium chloride, dehydrate, 0.210 g/L; magnesium chloride, hexahydrate, 0.043 g/L; potassium chloride, 1.162 g/L; potassium dihydrogen orthophosphate, 0.354 g/L; potassium thiocyanate, 0.222 g/L; sodium citrate, 0.013 g/L; sodium hydrogen carbonate, 0.535 g/L; disodium hydrogen orthophosphate, 0.375 g/L; pH, 6.8) at 37±2°C for one week, one, four and eight months. The percentage absorption and solubility were determined by Kazanji and Watkinson as follows:

Percentage sorption: $\left(\frac{W_2 - W_3}{W_1}\right)$ X 100%

Percentage solubility: $\left(\frac{W_1 - W_3}{W_1}\right)$ X 100%

Where W_1: the initial weight; W_2: the weight after absorption; W_3: the final weight after desiccation.

Water sorption values of Softic-49, Coe-Super-Soft, Coe Soft, Molloplast-B® and Flexibase in distilled water were 3.58%, 4.27%, 3.34%, 0.43% and 11.41%, respectively. In artificial saliva, fluid sorption values of Softic-49, Coe-Super-Soft, Coe Soft, Molloplast-B® and Flexibase were 0.71%, 1.45%, 1.15%, 0.52% and 6.55%, respectively. The apparent absorption values in artificial saliva were lower than in distilled water. Solubility values of Softic-49, Coe-Super-Soft, Coe Soft, Molloplast-B® and Flexibase in distilled water were 1.07%, 0.94%, 3.33%, 0.28% and 1.31%, respectively. In artificial saliva, solubility values of Softic-49, Coe-Super-Soft, Coe Soft,

Molloplast-B® and Flexibase were 5.79%, 6.02%, 5.30%, 0.07% and 2.69%, respectively. The solubility data in artificial saliva were larger than in distilled water. If we add the percentage absorption and the percentage solubility together to give real percentage uptake, the values in distilled water would be 4.64%, 5.21%, 6.67%, 0.71% and 12.72%, respectively. Total percentage uptake in artificial saliva for Softic-49, Coe-Super-Soft, Coe Soft, Molloplast-B® and Flexibase were 6.50%, 7.47%, 6.45%, 0.59% and 9.24%, respectively.

With the exception of Molloplast-B®, all the denture soft lining materials showed a lower percentage absorption in artificial saliva than in distilled water. For Molloplast-B®, the difference in the percentage solubility between artificial saliva and distilled water failed to show a significant difference. For the other denture soft lining materials, the solubility in artificial saliva was significantly higher than in distilled water. It was suggested that the filler present in Molloplast-B® is responsible for the water absorption characteristics but the type of filler was not investigated. No explanation was given for the length of the test period which at up to eight months did not seem long enough to characterize the expected life of materials. Kazanji and Watkinson (1988) were the first to compare cold-cured and heat-cured methacrylate-based denture soft lining material and silicone-based denture soft lining material in distilled water and artificial saliva although they did not discuss the potential reasons for the different findings.

Kawano *et al.* (1994b) measured the water sorption and solubility of 12 laboratory-processed denture soft lining materials using the American Dental Association (ADA) specification No.12 (ADA, 1975) for denture base polymers. Disk-shaped specimens, 50 mm in diameter by 0.5 mm thick, were dried in a desiccator containing anhydrous calcium sulphate until a constant weight was obtained. The disks were then immersed in 50 ml of distilled water at 37±1°C for 7 days, 1, 3, 6 and 12 months. They calculated the water sorption and solubility by ADA specification No. 12 for denture base polymers measuring water and solubility in mg/cm^2 where,

$$\text{Sorption } (mg/cm^2) = \frac{(W_2 - W_1)}{\text{Surface area}}, \quad \text{Solubility } (mg/cm^2) = \frac{(W_1 - W_3)}{\text{Surface area}}$$

They reported that only Molloplast-B® met the sorption value of 0.8 mg/cm^2 in ADA specification No.12. Kawano *et al.* selected ADA specification No.12 as a reference because there is no ADA specification for denture soft lining materials. Meanwhile, the sorption and solubility of an ideal denture soft lining material should be similar to that of the denture base material to avoid stress at the bonded junction.

However, for the ADA specification No.12, the specimen's surface is imperfect due to the traditional stone investment curing method, so the actual surface area is expected to be larger than the mathematically calculated area, which will add an additional variable to the results.

Waters *et al.* (1996) investigated the reason for high water absorption by room temperature vulcanizing (RTV) silicone denture soft lining materials. A variety of formulations of the polycondensation reaction experimental materials were devised in order to try to determine the cause of the high water sorption values. The constituents of experimental polydimethylsiloxane RTV rubber were polymer (hydroxyl end-blocked polydimethylsiloxane), filler (pyrogenic hydrophobic silica filler), catalyst (dicarboxylate tin) and cross-linker (mixture of alkoxy silanes). Disk-shaped specimens, 45 mm in diameter and 1 mm thick, were immersed in distilled water at 37°C for up to 23 months. They reported the original experimental material had excellent mechanical properties but would be unsuitable for clinical use because of its high water sorption values (22.71%) and large associated dimensional change (25.76% volume change). A formulation without filler showed a greatly reduced water absorption (4.28%) and volume change (-1.2%). The authors demonstrated the pyrogenic silica filler was the major cause of high water absorption but no explanation why its hydrophobicity caused high water absorption.

In 1997, Parker *et al.* reported the percentage uptake and percentage solubility of denture soft lining materials in distilled water and saline solutions. The materials they investigated were Novus and two experimental butadiene/styrene methacrylate elastomers which used either benzoyl peroxide or lauryl peroxide as an initiator. Specimens (20 by 40 by 1 mm) were immersed in distilled water, 0.45 or 0.9 M saline at

37°C for 196 days. Percentage uptake and solubility was calculated as a percentage of the initial weight. Real percentage uptake was calculated as the sum of percentage uptake and percentage solubility. The methods were different from previous studies and were determined as follows:

$$\% \text{ Uptake} = \left(\frac{W_t - W_0}{W_0} \right) \text{ X } 100, \qquad \% \text{ Solubility} = \left(\frac{W_0 - W_d}{W_0} \right) \text{ X } 100$$

Real % Uptake = % Uptake + % Solubility

Where W_0 = initial weight, W_t = weight at time t and W_d = final minimum desorbed weight.

Parker *et al.* (1997) found none of the specimens in distilled water reached equilibrium within a short time. The sorption and solubility data exhibited in distilled water was higher than in the other solutions, and in 0.45 M saline being approximately twice that in 0.9 M saline. These results were contrary to those found by Kazanji and Watkinson (1988a) who reported higher solubility in artificial saliva than in distilled water. Meanwhile, the specimens of the two experimental butadiene/styrene methacrylate elastomers showed a minus percentage solubility in 0.9 M saline, but no explanation was offered for this phenomenon. As previously described, as the osmotic pressure of the external solution is higher than that of distilled water, the difference between the internal droplet and the external solution will be lower. This will results in a reduced driving force for the growth of the droplets leading to lower uptake. Parker *et al.* confirmed the theory that the higher water uptake of elastomers is osmotically driven.

Hekimoğlu and Anil (1999) reported the sorption and solubility properties of two silicone-based denture soft lining materials (heat-cured Molloplast-B® and cold-cured Ufi Gel P) in relation to an aging process. One group of disk-shaped specimens, 50 mm in diameter by 0.5 mm thickness, was subjected to 900 hours (37.5 days) of simulated accelerated aging in a Weather-Ometer instrument. The Weather-Ometer instrument exposed the samples to continuous UV and visible light, a 110°F environmental temperature, and a programmed cycle of 18 minutes of distilled water spray within each 2-hour period. A second group of disks were only dried in a desiccator containing anhydrous calcium sulphate until a constant weight was obtained. Then the two groups of

disks were immersed in 50 ml of distilled water at 37±1°C for 15 and 30 days. They also used the ADA specification No.12 method to calculate sorption and solubility data. The solubility for Molloplast-B® and Ufi Gel P decreased after 30 days. Molloplast-B® and Ufi Gel P had smaller sorption at 30 days than 15 days. Negative increase in solubility was reported after the aging process. Water retention or changes in chemical structure were suggested as possible explanations for these results but both proposals still need to be investigated.

The same year, Parr and Rueggeberg (1999) reported the water sorption and solubility of a methacrylate-based denture soft lining material (PermaSoft®, which has the same formulation as EverSoft®). Bar-shaped specimens (44 mm x 8.5 mm wide x 1.2 mm thick), were immersed in distilled water at 37°C for 1, 7 or 30 days, and 6 and 12 months. They calculated water sorption by the following formula:

Sorption: $\left[\frac{(W_w - W_d)}{W_d}\right] \times 100$, Solubility: $\left[\frac{(W_p - W_d)}{W_p}\right] \times 100$

Where W_w = wet weight, W_d = desiccated weight and W_p = pre-immersion weight.
From day 1 to one month of immersion, no difference in weight was observed indicating a balance between water sorption and loss of solution components. However, after six months, sorption values more than doubled. Sorption values after one year were significantly greater than the 6 months values. From one day to one year, the results of 'resin-solubility analysis' ranged from 10% to 15%. The duration of water storage significantly influenced resin dissolution. Previous workers (Ellis *et al.*, 1979; Braden and Wright, 1983) have suggested the specimens used in sorption and solubility should be flat and thin in shape. The bar-shaped specimens may not be suitable for testing because the complexity of the shape may have unexpected consequences. Meanwhile, the term 'resin-solubility' used by the author is confusing since it is not the resin that is leached into the immersing fluid.

One year later, El-Hadary and Drummond (2000) reported on the water sorption and solubility of a methacrylate-based denture soft lining material (PermaSoft®) and a heat-cured silicone-based denture soft lining material (Luci-Sof) in distilled water. Specimens,

45 mm in diameter by 1 mm in thickness, were immersed in 250 ml distilled water at 37°C for one, four and six weeks. They used the Kazanji and Watkinson (1988) method to calculate percentage sorption and solubility. Water sorption and solubility values of PermaSoft® ranged from 0.58% to 2.49% and 0.74% to 2.05%, respectively. Water sorption and solubility values of Luci-Sof ranged from 0.08% to 0.41% and 0.04% to 0.47%, respectively. Obviously, as often reported, the water sorption and solubility of the methacrylate-based denture soft lining material was larger than that of the silicone-based denture soft lining material.

In 2002, Parr and Rueggeberg reported on the water sorption and solubility of two silicone-based denture soft lining materials; one heat-cured type (Luci-Sof) and the other cold-cured product (Tokuyama). Bar-shaped specimens (44 by 8.5 by 1.2 mm thick) were immersed in distilled water at 37°C for one day, one week, one month, six months, and one year. They used their previous method (Parr and Rueggeberg, 1999) to determine the water sorption and solubility. Water sorption and solubility values of Luci-Sof ranged from 0.40% to 1.25% and 0.40% to 1.15%, respectively. Water sorption and solubility values of Tokuyama ranged from 0.70% to 1.10% and 0.40% to 0.68%, respectively. They failed to show a significant difference in sorption values between heat-cured Luci-Sof and cold-cured Tokuyama after six months and after one year of water storage. Moreover, at all time intervals after one week, significantly lower solubility was observed for the cold-cured Tokuyama than for the heat-cured Luci-Sof. Parr and Rueggeberg recommended using cold-cured Tokuyama over the heat-cured Luci-Sof because the former demonstrated more desirable or equivalent properties. However, these results were only recorded by immersion in distilled water, and achieving a uniform thickness of cold-cured denture soft lining material at the chairside is still very difficult. It also should be noted that the term 'resin-solubility' used by the author is confusing since in the silicone-type materials it is not the resin that is leached into the water.

In 2004, Yanikoğlu and Duymuş reported on two cold-cured methacrylate-based denture soft lining materials (Fixo-Gel and Visco-gel) and three silicone-based denture soft lining materials (cold-cured Mollosil® and Ufi Gel P, and heat-cured Molloplast-B®) reporting

their water absorption and solubility in different solutions. Specimens, 50 mm in diameter by 0.5 mm in thickness, were immersed in distilled water, artificial saliva (NaCl 0.400 g; KCl 0.400 g; $CaCl_2H_2O$, 0.795 g; NaH_2PO4, 0.69 g; $Na_2S.9H_2O$, 0.005 g; Urea 1.000 g; distilled water 1000 ml) and a denture cleansing solution (Fittydent cleansing tablets, FITTYDENT international GMBH A-7423 Pinkafeld, Austria) at 37±2°C for one, four and sixteen weeks. Yanikoğlu and Duymuş adjusted the artificial saliva pH with NaOH or HCl to try to simulate neutral, acidic and basic saliva. They also used the Kazanji and Watkinson (1988a) method to calculate percentage sorption and solubility. Unfortunately, they did not report their experimental data in detail, but exhibited their results by histograms. In comparing their figures, for the three silicone-based denture soft lining materials, there was low percentage absorption and solubility with differences between the results for immersion in the denture cleanser and the other solutions (distilled water, neutral, acidic and basic artificial saliva). Meanwhile, the test period was only up to sixteen weeks which seemed too short for the expected life of materials and therefore less likely to show the effects of immersion in different solutions.

León *et al.* (2005) evaluated the water sorption and solubility properties of two denture soft lining materials polymerized by different methods following thermocycling. They investigated one, Light Liner, polymerized by visible light, and the other, Ever-Soft®, processed by hot water and microwave energy. Disc-shaped specimens, 50 by 0.5 mm, were dried and weighed prior to thermocycling (2000 cycles) between water baths of 5°C and 55°C. After thermocycling, the specimens were weighed, and then dried to a constant weight to calculate the water sorption and solubility. The percentage water sorption and solubility were determined by the formula described by Kazanji and Watkinson (1988a). Water sorption and solubility values of Light Liner were 3.0% ± 0.9% and 5.3% ± 0.3%, respectively. Water sorption values of EverSoft® were 2.8% ± 0.6% (hot water bath), and 2.3% ± 0.8% (microwave energy). Solubility values of EverSoft® were 7.3% ± 1.1% (hot water bath) and 7.8 ± 0.9% (microwave energy). Their results were in contrast with those reported by El-Haldary and Drummond (2000) for PermaSoft® which is a similar material to EverSoft® (water sorption: 0.2% to 1.5% and solubility: 0.5% to 2.0%). These

different studies used different methods and materials and it is not possible to identify the potential effect of thermocycling since no internal controls were used.

In all previous studies of sorption and solubility, there were four different methods of calculating the percentage uptake, Kazanji and Watkinson (1988a), Kawano *et al.* (1994b), Parker *et al.* (1997) and Parr and Rueggeberg (1999). The differences focus on (1) combined initial desiccated weight and final desiccated weight used to calculate sorption (Kazanji and Watkinson, 1988a); (2) surface area used to calculate sorption (Kawano *et al.*, 1994b); (3) initial desiccated weight used to calculate sorption (Parker *et al.*, 1997); (4) final desiccated weight used to calculate sorption (Parr and Rueggeberg, 1999). Using the surface area in the calculation is not practical, because it is difficult to measure the surface area of a specimen perfectly due to irregular shapes of specimens and surface roughness factors and further sorption is a bulk phenomenon not a surface effect. Calculation on the desiccated weight to get the sorption value may cause an error. The uptake measurement is a combined fluid uptake and loss of soluble components. The specimen is desiccated initially to remove the small amount of water present following the fabrication process. The specimen is desiccated finally to remove the total amount present following the sorption process. Using the initial desiccated weight to calculate the percentage weight uptake is more reasonable than the final desiccated weight since this will be influenced by loss of soluble components.

From these extensive studies we may conclude, firstly, longer aging times did result in significantly greater sorption and/ or solubility than shorter aging times. Secondly, a specimen in the form of a thin flat disc should be used, so that water transport is sensibly only in one direction through the major surfaces; this simplifies the theoretical analysis of the data.

2.3.2 Mechanical hardness characteristics

Hardness testing has its origins in metallurgy, because it affords a quick, easily applied test useful for quality control testing, and simple classifications (e.g., dental gold alloys were classified according to hardness ranges) (Murray, 1993). Although, hardness is

defined by the American Society for Testing and Materials (ASTM) as the resistance to indentation as measured under specified conditions, the term may also refer to the resistance to scratching, abrasion or cutting. Hardness testing usually falls into three main categories; scratch, dynamic and static indentation hardness.

a) Scratch hardness is one of the oldest forms of hardness measurements and is based on the ability of one solid to scratch or resist the surface of another (Tabor, 1951; Callister, 2003).

b) Dynamic deformation or indentation apparatus employ an indenter that is dropped from a specified height onto the test specimen surface, and the hardness value can be determined from the height of rebound of the indenter or expressed in terms of energy of impact and the size of the remaining indentation (Tabor, 1951). The Shore Scleroscope is one of the best known examples, where the height of rebound of an indenting hammer is read off against a scale calibrated in equal arbitrary units (O'Neill, 1934).

Static indentation tests are more commonly used and are associated with particular indentation geometries. Many of the apparatus used to determine hardness values produce, under a specified load, an indentation in the material, and what is measured appears to be the resistance of the material to plastic flow (Lea, 1936). The depth or size of the resulting indentation is related to a hardness number (Callister, 2003). The types of tests used with accuracy by the metal industry involve; the Brinell (steel ball indenter) hardness tests, Rockwell (ball or metal cone indenter) hardness test, Vickers (square-based diamond indenter) and Knoop (pyramid diamond indenter) microhardness tests. Under controlled conditions, these tests determine the depth of penetration of a non-deformable indenter for a given load within a specified period of time. The hardness value is related to the degree of permanent deformation produced in the test specimen (McCabe, 1990). The Durometer is a popular instrument for measuring the indentation of rubber and rubber-like materials. The preferred tester for softer and harder materials are the respective Shore A and Shore D scales, and is a convenient means of classifying rubber materials. The Shore hardness test is a useful measure of relative resistance to indentation of various grades of polymers

and meets the international test standards set by the International Organisation for Standardisation (ISO). The Shore hardness test essentially consists of a flat ended indenter to measure penetration depth caused by delivering a constant load using a calibrated spring.

According to ISO standards, the penetration of an indenter bears a known relation to Young's modulus (E) of a rubber. Young's or elastic modulus is defined as the measure of the elastic force of any substance, expressed by the ratio of a stress on a given unit of the substance to the accompanying distortion, or strain (Treloar, 1958).

Hence, hardness testing is preformed frequently since it is simple, inexpensive, non-destructive, and can be transformed to mechanical properties, such as tensile strength (Callister, 2003).

In 1961, Travaglini *et al.* investigated the Shore A hardness of ten early denture soft lining materials determined after curing and at intervals after storage in distilled water at 25°C for 12 weeks. The thickness of the test specimens was 2 mm and they were placed on a glass slab for testing. The initial hardness values were from 33 to 85. After 12 weeks immersion at 25°C in distilled water, they found products plasticised with alcohol had a rapid increase in hardness, while other methacrylate-based materials which used other plasticisers, showed less rapid changes in hardness. However, the temperature of 25°C did not simulate oral condition (37°C) and the period of study seemed too short to represent normal clinical use.

Craig and Gibbons (1962) repeated the previous work of Travaglini *et al.* (1960) to report the Shore A hardness of the same early denture soft lining materials in distilled water at 25±1°C for 20 weeks. In spite of a further eight weeks immersion at 25±1°C in distilled water, their results were similar to those of Travaglini *et al.* (1960). They found the major changes in hardness on storage in distilled water took place within two to four weeks after immersion.

Eick *et al.* (1962) repeated the previous work of Travaglini *et al.* (1960) but the specimens were immersed in distilled water at 37°C for one month. They found the Shore A hardness in water at 37°C was much less than the hardness values in water at 25°C except for two silicone products. They speculated the major softening was due to the increase in temperature which is logical because the temperature was above the glass transition temperature. However, the period of study was still too short to represent normal clinical use.

Louka *et al.* (1977) designed two different methods for improving the wettability of denture soft lining materials. Their materials and method were described in section 2.3.1.2. Incidentally, they also evaluated the softness using a specially designed apparatus based on the British Standards test 930. They stated that the softness of the specimens was not affected by the wettability treatments to any degree. However the immersion period was so short that the results were predictable.

The hardness of a material depends to a certain extent on its thickness. The thickness of a denture soft lining material is critical in the effective softness. However, the optimal thickness of the lining material to be applied to the denture may be controversial. By clinical experience, Storer (1962) has stated that to recommend a standard thickness was difficult because a 1 mm thickness would be satisfactory with a soft material whereas a 3 mm thickness might be necessary with the harder materials. By research, Wright (1976) and Kazanji and Watkinson (1988b) recommended a thickness of a denture soft lining material of 1.8-3 mm as most appropriate.

Qudah *et al.* (1991) investigated the effect of thermocycling on the hardness of denture soft lining materials. The thickness of the test specimens was 3 mm bonded to 3 mm thick PMMA denture base. Test specimens were thermocycled between 18±1°C and 53±1°C. The specimens were measured at 1, 7, 14, and 28 days after thermocycling. The methacrylate-based denture soft lining materials were initially very soft, but hardened significantly after seven days. It was thought that leaching out of plasticisers was responsible for the hardening of methacrylate-based denture soft lining materials.

Dootz *et al.* (1992) investigated hardness of eleven denture soft lining materials using a Shore A hardness instrument, with 10 mm thick specimens. The investigators found a wide range of hardness values from 25 to 95 Shore A units, which provided clinicians with a choice of materials. The following year, the same authors (Dootz *et al.*, 1993) compared the same physical properties of the same denture soft lining materials using a Weather-Ometer accelerated ageing device. An increase in the tensile strength of the methacrylate-based denture soft lining materials after accelerated ageing was assumed to be due to continuing polymerisation and loss of plasticiser. The high percentage elongation and low Shore A hardness values observed for the silicon-based denture soft lining materials contrasted with those for methacrylate-based denture soft lining materials (lowest elongation and highest hardness values). It was concluded that accelerated ageing considerably affected physical properties.

Sealing of denture soft lining materials has been recommended for maintaining softness and extending longevity. Yoeli *et al.* (1996) reported the hardness of four autopolymerised methacrylate-based denture soft lining materials and two silicone-based denture soft lining materials (Table 2.2) after immersion in water at 1, 7 14, 21, 28 and 54 days. Softness was assessed with a Shore A durometer. The softness of three of four methacrylate-based denture soft lining materials (except PermaSoft®: supplied by Dentsply Austenal International., USA, is the American brand name for EverSoft®) changed with time, unlike the silicones whose softness remained consistent. The stable softness of PermaSoft® groups showed that for a short period of time, the material can be used in the mouth without the need for a surface sealer.

Table 2.2 Denture soft lining materials assessed for hardness by Yoeli *et al.*, 1996

Material	Polymerisation mode	Manufacturer
Coe Soft™	Autopolymerising	GC, USA
Flexacryl™	Autopolymerising	Lang, USA
Permasoft®	Autopolymerising	Nu-Dent, USA
Permasoft® + sealer	Autopolymerising	Nu-Dent, USA
Lynal™	Autopolymerising	Dentsply
Molloplast-B®	Heat curing	Detax, Germany
Permaflex™	Heat curing	Kohler, Germany

*PermaSoft® is the same formulation as EverSoft®.

Petropoulos *et al.* (1998) investigated hardness of four autopolymerising denture soft lining materials (Tokuyama Soft Reline™, Coe-Comfort™, PermaSoft®, and Total-soft™)

after immersion in artificial saliva, Efferdent™ denture cleanser, Efferdent™ denture cleanser with a soft brush, ethanol, and sodium hydroxide at 0, 1, 3, 7, 30 and 90 days. A sealer was applied to half of the specimens. The sealed samples were compared with unsealed samples. They found the application of sealer did not significantly change the hardness before immersion but sealed samples showed greater durability by maintaining greater than 50% of their initial hardness for 30 days. Ethanol showed a strong softening effect with greater than 50% decrease in hardness after one day immersion of the unsealed samples. The sealed and unsealed silicone-based denture soft lining material (Tokuyama Soft Reline™) remained unaffected through the immersion period. They suggested that the sealer played an important role in the preservation of the softness of methacrylate-based denture soft lining materials.

Canay *et al.* (1999) reported hardness changes of three denture soft lining materials immersed in three food colourant solutions. The denture soft lining materials were heat-cured silicone type Molloplast-B® and Flexor, and heat-cured plasticised acrylic type Coe Super Soft. Three commonly used food and beverage colorants (erythrosine, tartrazine and sunset yellow) were investigated. Specimens, 50 by 10 by 2 mm, were immersed in 3% w/v erythrosine, tartrazine and sunset yellow unchanged solutions at unknown temperature for up to six months. Specimens were tested two hours after sample preparation and at intervals of one, three, and six months after storage in colorant solution. Shore A hardness values of heat-cured Molloplast-B® and Flexor ranged from 44 to 46 and 39 to 41, respectively. For both the hardness changed little. Coe Super Soft values ranged from 89 to 95 and were fairly hard from the beginning to the end. Unfortunately, the authors did not clearly address the test temperature. Moreover, these colorants are only used at 0.02-0.1% level in foods, and this low level of colorants may increase the development of stain but may not equally the effect of food and oral fluids.

Tan *et al.* (2000) reported the effects of denture cleansers and temperature on Molloplast-B® hardness. The denture cleansers were three perborate-containing cleansers (Efferdent, Polident, and Kleenite), one persulfate-containing cleanser (Sparkle-Dent), and one hypochloride product (Javex/Calgon). Specimens were fabricated in the form of a 25 x 50

x 6 mm rectangular shape. One-half of the thickness consisted of heat-polymerised denture base acrylic (Lucitone 199) and the remaining 3 mm consisted of Molloplast-B®. Specimens were immersed in distilled water at 25°C (room temperature) or 55°C (household hot tap water) for 4 ½ months. The solutions were replaced twice a day. To simulate the real situation, the solutions at 55°C were allowed to cool down naturally once the specimens were immersed. The hardness was measured using a Shore A durometer. The initial and final hardness values at 25°C were from 49.78 to 50.96, and from 49.10 to 50.04, respectively. The initial and final hardness values at 55°C were from 50.36 to 51.42, and from 48.54 to 49.84, respectively. Neither denture cleansers nor temperature changed the hardness values significantly. The methods used were more aggressive than normal everyday cleansers but still the effects on Molloplast-B® were limited.

In 2001, Polyzois *et al.* reported the long-term hardness of two methacrylate-based denture soft lining materials (autopolymerising EverSoft® and heat-cured Supersoft™) after immersion in distilled water. The hardness was measured at day 0, then every month for one year. They found EverSoft® remained softer than Supersoft™ during the storage period. They also found EverSoft® and Supersoft™ hardened during the first month of immersion and thereafter followed a similar pattern with no significantly change in hardness. They suggested the application of surface sealer was effective in maintaining softness for EverSoft®.

In 2002, Parr and Rueggeberg reported on the hardness of two silicone-based denture soft lining materials; one heat-cured type (Luci-Sof) and the other a cold-cured product (Tokuyama). Disk-shaped specimens, 31 mm in diameter by 10 mm thick, were immersed in distilled water at 37°C for up to one year. Hardness values were obtained using a Shore A Durometer. Specimens were tested immediately and after storage in distilled water at 37°C for durations of one day, one week, one month, six months, and one year. Shore A hardness values of heat-cured Luci-Sof and cold-cured Tokuyama ranged from 42 to 48 and 19 to 30 respectively. Shore A hardness values of the heat-cured Luci-Sof were greater than the cold-cured Tokuyama at each time interval after

polymerization. Moreover, Shore A hardness values of the cold-cured Tokuyama remained constant after one week of storage, whereas hardness values for the heat-cured Luci-Sof increased with immersion duration. However, these results were recorded only by immersion in distilled water, and may not really reflect the oral conditions.

2.3.3 Surface roughness characteristics

Roughening of the denture soft lining material surface is common and is the most common reason given for replacement of a denture soft lining material because of loss of surface detail (Wright, 1984).

The repeated sorption and desorption of water from the surface of the denture soft lining material may be one factor in producing roughening of the surface (Schmidt and Smith, 1983b; Wright, 1984 and 1986; Braden *et al.,* 1995). Other factors which influence this are thought to be some of the constituents of foods and drinks, such as essential oils (Jepson *et al.,* 1993a) certain denture cleansers (Schmidt and Smith, 1983b; Wright, 1984) and the effect of surface contamination by *C. albicans* (Mäkilä and Hopsu-Havu, 1977; Mäkilä and Honka, 1979; Braden *et al.*, 1995). The effects of denture cleansers on the properties of denture soft lining materials have also been studied (Davenport *et al.*, 1986; Nikawa *et al.*, 1994). Certain denture cleansers have been reported to result in considerable deterioration of short term denture soft lining materials giving rise to roughened surfaces within a relatively short time, which may thus lead to colonisation by micro-organisms. The increased porosity of denture soft lining materials can lead to plaque accumulation and *C. albicans* colonisation. Some denture cleaners can cause significant deterioration of denture soft lining materials because they can cause loss of soluble components and plasticisers.

Nikawa *et al.* (1994) examined the surface porosity and distortion of several commercial denture soft lining materials under conditions representative of a normal overnight cleansing regime compared to those of standard samples immersed in distilled water. Various types of denture cleansers exist on the market, and their composition and pH can

differ from ones that contain alkaline peroxides, enzymes or acids to ones that are detergents or typical everyday mouth rinses.

In Nikawa and his colleague's investigation, they found that on the whole, those cleansers that contained peroxide seemed to perform the worst, where short term denture soft lining materials suffered from a greater deterioration compared to the other cleansers. They failed to show a significant correlation between the pH of the denture cleanser and the severity of deterioration suffered by the denture soft lining material.

In 2000, Zissis *et al.* reported a study into roughness of denture materials. They investigated the roughness of twenty commercial denture materials. Four denture base resins, nine hard lining materials, and seven denture soft lining materials were evaluated for roughness (Table 2.3).

Table 2.3 Denture soft lining materials assessed for roughness by Zissis *et al.*, 2000.

Material	Polymerisation mode	Manufacturer
Perform Soft™	Visible-light curing	Whaledent
Light Liner Soft™	Visible-light curing	HJ Bosworth
Resiline™	Visible-light curing	Dentsply/DeTrey
Astron™	Visible-light curing	Astron
Mollosil®	Autopolymerising	Detax
Mollosil® + varnish	Autopolymerising	Detax
Molloplast-B®	Heat curing	Detax
Molloplast-B® + varnish	Heat curing	Detax
Permaflex™	Heat curing	Kohler
Permaflex™ + varnish	Heat curing	Kohler

Zissis *et al.* (2000) measured roughness using Mitutoyo Surftest SV-400, a conventional stylus profilometer which scans the surface using a diamond stylus under a constant load and computes the numeric values representing the roughness of the profile. The mean arithmetic roughness values (R_a) obtained were used for the comparisons. The results were as follows:

1. The overall R_a values ranged from 0.7 to 7.6 μm.
2. The denture base materials group exhibited R_a values from 3.4 to 7.6 μm, and the hard liners were from 0.7 to 4.4 μm.
3. The autopolymerised and visible-light cured denture soft lining materials presented R_a values from 0.7 to 3.5 μm, and the heat-cured types ranged from 3.5 to 4.0 μm.

4. The varnished denture soft lining materials exhibited R_a values from 2.8 to 4.1 μm, and the unvarnished ones were from 3.2 to 4.0 μm.

The R_a value of Molloplast-B® without varnish was 3.5 μm, which was higher than the results reported by Loney and Moulding (0.6 μm) (Loney and Moulding, 1993) and Veres *et al.* (1.5 μm) (Veres *et al.*, 1990). Zissis *et al.* thought these differences were the result of the different surface texture of the specimens caused by processing against different materials. The R_a value of Molloplast-B® with varnish was 4.1 μm, which was greater than the unvarnished group. This is despite that the application of the varnish supplied by the manufacturers as a finishing procedure after curing is recommended to smooth out the roughness of the material. Zissis *et al.* (2000) confirm that the application of varnish decreased the roughness of Permaflex™ and Mollosil® denture soft lining materials.

Tan *et al.* (2000) reported the effect of denture cleansers and temperature on Molloplast-B® texture. Their materials and method were described in section 2.3.2. The R_a was measured using a contact stylus method. The initial and final R_a values after immersion for four weeks at 25°C were from 33.20 to 52.62 (μm) and from 42.28 to 56.00 (μm), respectively. The initial and final R_a values after immersion for four weeks at 55°C were from 37.74 to 51.42 (μm), and from 47.82 to 69.32 (μm), respectively. Both denture cleansers and temperature failed to show significant effect on the R_a values, although the differences between the initial R_a values made comparison difficult. Moreover, the R_a value may be an aberrant estimation because of the use of a contact stylus on the elastic surface. Again, the aggressive denture cleanser treatment did not cause deterioration of the Molloplast-B® surface.

Jin *et al.* (2003) reported the changes in surface roughness of soft lining materials caused by chemical denture cleansers measured also using a contact stylus method. The denture soft lining materials and the denture cleansers are listed Table 2.4. They investigated one denture base resin, two autopolymerising methacrylate-based denture soft lining materials, four autopolymerising and one heat curing silicone-based denture soft lining materials by immersion in five denture cleansers and distilled water for up to 180 days.

The specimen surface was boxed using wax, and poured with the Die-Stone for indirect measurement. With respect to measurement, they reproduced the surface detail by using stone, but the deep surface features and bubbles on the stone surface as a result of pouring may cause an error.

Table 2.4 Materials assessed for roughness by Jin *et al.*, 2003.

Material	Type of curing and materials
Bio resin	Heat-curing acrylic resin
Soften	Autopolymerising acrylic
Nissin Soft Reverse	Autopolymerising acrylic
Mollosil	Autopolymerising silicone
Evatouch (Soft type)	Autopolymerising silicone
Tokuyama Soft Relining	Autopolymerising silicone
GC Denture Relining	Autopolymerising silicone
Molloplast-B®	Heat curing silicone
Denture cleanser	**Type**
Steradent	Alkaline peroxide
Correct	Neutral peroxide
Polident	Neutral peroxide with enzyme
Pika DCE	Neutral peroxide with enzyme
Clean Soft	Enzyme

Almost all materials became rougher, to a greater or lesser extent, following immersion in denture cleansers. The enzyme denture cleansers tended to cause more severe changes. However, their R_a data showed the changes to be very small from 1.1 to 0 μm, and the original value of Mollosil was 1.0 μm. These were less than the results reported by Zissis *et al.* (2000) (3.0 μm) and these values may be an underestimation. Such underestimation could be when using a contact stylus on the material to be measurement.

Over or under estimation of the roughness of a surface may be caused if the surface to be measured is soft and elastic, and the deeper surface irregularities may be narrower than the stylus itself. The contact stylus may also damage the surface, and it may also produce an erroneous high value because the stylus has left the surface following rebound of the elastic material. These effects may be overcome by using an indirect method to reproduce the surface detail using a rigid material, and a narrow and longer stylus. In practice such a stylus would be weak and easily damaged. The use of a non-contact laser stylus would reduce these problems. However, these also have some difficulties because of the reflectivity of the surface.

2.3.4 Wettability characteristics

All of the polymers used as denture soft lining materials are essentially hydrophobic. However, denture soft lining materials should ideally be wetted by saliva, so that a lubricating layer can be set up between the material and the mucosa thus reducing frictional problems leading to patient discomfort. The layer of saliva wetting the surface may also increase the retention. The problem of poor wettability has been particularly associated with silicone-based denture soft lining materials (Wright, 1980a). Hence, how to improve the wettability of the denture soft lining material is an interesting topic to increase patient comfort.

In 1965, O'Brien and Ryge reported improved wettability of a conventional acrylic denture base by applying a thin film of silicon tetrachloride to the surface. The denture retention was improved by approximately 14%.

In 1977, Louka *et al.* designed two different methods for improving the wettability of denture soft lining materials. The two methods were: (1) a paint-on technique for depositing a thin film of silicon tetrachloride on the surface, (2) a modification of a vacuum discharge treatment by CASING. They measured the contact angle to determine wettability. The commercial materials tested have been described earlier. The authors showed both the silicon tetrachloride and the CASING-hydroxyl methods were significantly effective in reducing the contact angle; however the effect did not extend over a period longer than two weeks due to the water sorption which was significantly increased.

Polyzois *et al.* (1991) modified a maxillofacial silicone rubber material by the incorporation of various silicone alkene oxide block co-polymers directly into the polymeric matrix. Some of the surfactants proved to reduce the contact angle, but the long-term stability and the effect on material behaviour were not reported.

Waters and Jagger (1999) modified an experimental silicone rubber denture soft lining material by the addition of different quantities of polyalkylene oxide

poly(dimethylsiloxane) surfactants directly into the polymeric matrix. The material modified with surfactants showed improved wettability compared to the unmodified material. However, there was no examination of how these additions would affect the other properties of the soft lining.

2.4 Polymer degradation

2.4.1 Definitions

With regard to materials composed of synthetic macromolecules, the term polymer degradation is used to denote "*changes in physical properties caused by chemical reactions involving the chain scission process in the backbone during which polymer chains are cleaved to form oligomers and finally to form Monomers*" (Göpferich, 1996). In linear polymers, these chemical reactions lead to a reduction in molecular weight, i.e. to a diminution of chain length. So, polymer degradation is frequently described by chemical bond scission reactions in macromolecules. However, there are several ways to induce degradation of polymers by chemical, mechanical, photochemical, thermal, radiation-chemical or biological means (Schnabel, 1981; Göpferich, 1996).

Polymers used in dentistry which are subjected to degradation include the filling materials such as composites or glass ionomer cements, crown and bridge materials such as veneering materials or plastics for temporary restorations, polymers needed for maxillofacial reconstructions and polymers for the construction of full and partial prostheses. Degradation of dental polymers will lead to increased wear, fractures due to increased brittleness, and discoloration (Roulet, 1987).

2.4.2 Simple mechanism

There are two main mechanisms which may cause a release of substances from polymeric materials: (i) unbound monomers and/or additives are eluted by solvents after setting; and (ii) leachable components are created by degradation or erosion over time (Göpferich, 1996). Erosion is a complex process. Water or other solvents enter the polymer bulk, which may result in swelling. The intrusion of water or a solvent triggers the chemical degradation. Progressive degradation changes the microstructure of the bulk through the

formation of pores, via which residual monomers, degradation products and additives are released. Concomitantly, the pH inside pores begins to be controlled by degradation products, which typically have some influence on the pH of the fluid in contact with the material. Finally, materials may be released at the surface, leading to erosion with weight loss of the polymer (Göpferich, 1996).

Polymer degradation is the key process of erosion. To classify degradable polymers a distinction is made between surface (or heterogeneous) and bulk (or homogeneous) eroding materials (Figure 2.28). During an application, surface eroding polymers lose material from the surface only. They get smaller but keep their original geometric shape. For bulk eroding polymers, degradation and erosion are not confined to the surface of the material only. Therefore, the size of the material will remain constant for a considerable portion of time during its application. The advantage of surface eroding polymers is the predictability of the erosion process. This is desirable when using this polymer for drug delivery, where the release of drugs can be related to the rate of polymer erosion (Göpferich, 1996), but it seems undesirable when using this material for a denture soft lining material because of degradation, swelling, the dissolution and diffusion of leachable substances, morphological changes, and creation of an environment for potential bacterial and yeast growth.

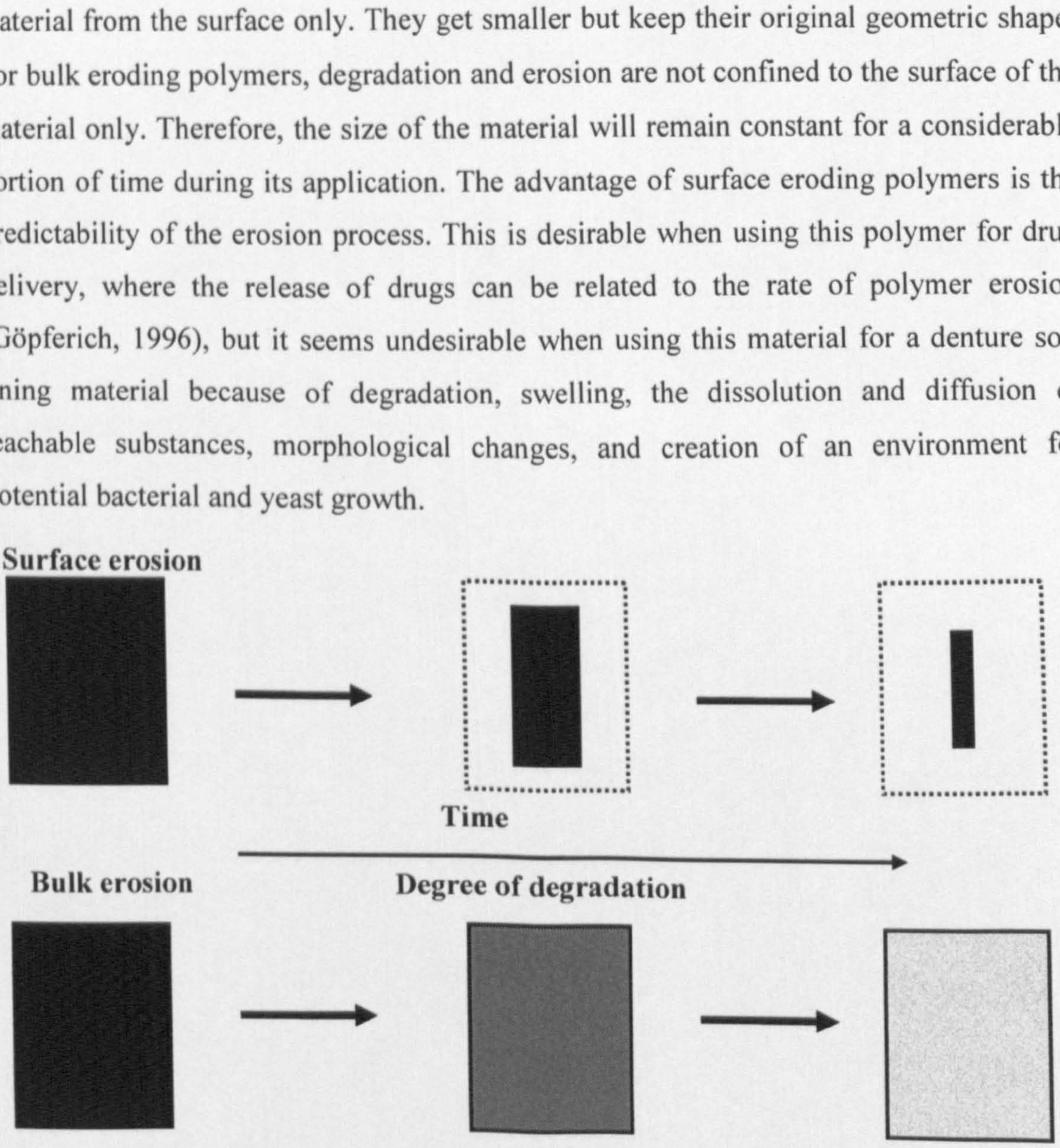


Figure 2.28 Schematic illustration of surface erosion and bulk erosion (adapted from Göpferich, 1996).

Oral and other fluids including organic solutions, may act as eroding materials and cause swelling and breakdown of denture soft lining materials which will cause long-term degradation.

2.5 Artificial saliva and food simulating solvents

2.5.1 Introduction

Intra-oral conditions are generally more complex than the typical laboratory condition since here the oral environment is simulated using distilled water. Dental materials may be exposed either intermittently or continuously to chemical agents, such as those found in saliva, food and beverages. Cyclical exposure occurs during eating or drinking (until the prostheses are cleaned). How to simulate the oral environment is the key to experimental design to evaluate and predict the behaviour of dental materials during function. The use of artificial saliva (AS) and food simulating liquids (FSLs) may help to simulate the oral environment *in vitro*.

2.5.2 Artificial saliva

The essential fluid in the oral environment is saliva. So, the design of testing *in vitro* should use natural saliva. Unfortunately, in the use of natural saliva *in vitro* to test dental materials it is very difficult to maintain qualitative and quantitative analysis. Therefore, the formulation of artificial saliva which represents as closely as possible natural saliva is recommended. This attempts to reproduce the chemical conditions pertaining in the mouth.

In 1931, Souder and Sweeney used artificial saliva to study mercury release from dental amalgam restorations. Fusayama *et al.* (1963) slightly modified a recipe from Swartz *et al.* (1958) (unreported) to evaluate the corrosion of dental gold and amalgam for six months. This Fusayama structure was later employed mostly for electro-chemical and biological tests on dental materials because it closely approximated natural saliva (Marek *et al.*, 1983).

2.5.3 Food simulating liquids

The food simulating liquids (Wu and McKinney, 1982; McKinney and Wu, 1985) or intra-oral dietary simulating solvents (Jepson *et al.*, 2000; Yap *et al.*, 2003) are used as food simulants. The selection of food simulating liquids was based on "U.S. Food and Drug Administration (FDA) Guidelines in 1976 (Table 2.5). 75% ethanol and heptane were the most used as food simulating liquids. In 2002, the FDA revised the guidelines on food simulating liquids. The liquids are listed in Table 2.6 with examples of the foods they are intended to simulate.

Table 2.5 Food simulating liquids (FDA, 1976)

Food-type	Recommended simulants
Water, light beverages, alcohol, candy, syrups, wine, beer	Ethanol in Water 100%, 75%, 50%, 25%, 0%
Vegetable oils, fats, meats	Heptane

FDA guidelines for chemistry and technology requirements of indirect additive petitions, Washington, DC: FDA, March, 1976.

Table 2.6 Food simulating liquids (FDA, 2002)

Food-type	Recommended simulants
Aqueous and acidic foods	10% ethanol[1]
Low- and high-alcoholic foods	10 or 50% ethanol
Fatty foods	Miglyol™ 812[2] or HB307[3]
1. 10% ethanol is intermediate in alcohol concentration between wine and beer. 2. Miglyol™ 812 is derived from coconut oil. 3. HB307 is a mixture of synthetic triglycerides, primarily C_{10}, C_{12}, and C_{14}.	

FDA/CFSAN Guidance for Industry – Preparation of Food Contact Notifications (2002).

Previous test protocols (FDA, 1988) recommended the use of water and 3% acetic acid as food simulants for aqueous and acidic foods, respectively. However, water and 3% acetic acid have been shown to underestimate migration into aqueous foods. Therefore, 10% ethanol is now recommended as an aqueous and acid food simulants (FDA, 2002). But, 3% acetic acid is still recommended as an acidic food stimulant by the EC Food Contact Legislation (2000).

A solvent effect acting clinically to encourage material chemical degradation is a possible explanation of the differences in clinical and laboratory degradation. Interestingly, there

is no information available in the literature regarding the effect of food simulating liquids on long-term denture soft lining materials under controlled laboratory conditions.

2.5.4 Solvent effect on resin based composites

Study of the degradation of resin has been carried out on many resin systems. Wu and McKinney (1982) investigated the wear of resin composite specimens (polymer based system) after immersion for two weeks in cyclohexane and various ethanol-water-mixtures: 100, 75, 50, 25 and 0% ethanol. They found that the investigated organic chemicals considerably increased the wear rate, due to a softening of the resin matrix. The mechanism proposed was that the solvents penetrated and expanded or swelled the polymer network, which facilitated the diffusion of unbound monomer and additives.

It is possible to predict the efficiency of a solvent for a given polymer by matching their solubility parameters. The solubility parameter describes the ease with which a molecule will penetrate and dissolve another substance, such as a polymer. The relative affinity of a polymer and solvent can be assessed using solubility parameters, which provides an easy numerical method of rapidly predicting the extent of interaction between materials, particularly liquids and polymers. They are useful in ensuring the suitability of polymers for practical applications and in formulating blends of solvents for particular purposes. The solubility for a given polymer in a given solvent is favourable if the solubility parameters of the polymer and solvent are equal (Van Krevelen, 1976).

Wu and McKinney (1982) showed the solvents with solubility parameters in the range of 9.0 to 14.5 $(cal/cm^3)^{1/2}$ were good solvents for resin composites, having the capacity to penetrate and soften them. This led to the use of various chemicals as FSLs. Such chemicals appear in FDA guidelines for additives to food. Wu and McKinney determined that ethanol solutions had similar solubility parameters to dimethacrylate polymers and were clinically relevant solutions for dentistry. In particular, the use of solution containing 75% ethanol/water was the best solvent for composites.

Wu *et al.* (1984) reported that clinically damaged resin based composite restorations had altered layers on both non-stress-bearing and on stress-bearing occlusal surfaces. It was speculated that the chemical or thermal environment contributed to the *in vivo* degradation of these materials. The observed surface damage was attributed to softening and removal of portions of the polymer matrix by chemicals in the oral environment. Since the resin phase of this material is a dimethacrylate resin, it is reasonable to assume that the effects could be even greater in a methacrylate-based denture soft lining material.

Ferracane and Condon (1990) compared the rate of elution from a microfilled composite using water and a 75% ethanol-water mixture. They found that 50% of the leachable components were extracted by water within three hours, but 75% by the ethanol-water mixture. After 24 hours, nearly all leachable substances (unbound monomers and oligomers) were eluted. After a seven days period, 1.5-2.0% of the initial weight of the specimens had been extracted. They concluded that a polymerised composite does not provide a long-term source for leachable components.

Ferracane (1994) stated that the intra oral fluids represent solvents probably lying somewhere between the more aggressive organic solvents and water, which is less effective than pure ethanol.

Lee *et al.* (1995) stored hardened specimens from three commercial dental resin composites in two different fluids: 75% ethanol-water-mixture as a food simulator and artificial saliva. The specimens were stored at 37°C for 7, 14, and 30 days. Analysis of the released components from the resin specimens was performed by means of FTIR (Fourier-Transform-Infrared-Spectroscopy). No elution was found in the artificial saliva, even after 30 days. However, Lee *et al.* found 75% ethanol/ water did affect the resin specimens. They reported ethanol degradation of resin occurring via reductions in the amount of aliphatic C=O and O-H bonds and increases in C=O groups. They also suggested the FTIR was a very useful and practical method for the analysis of structure of material taken from the specimens. Lee *et al.* (1995) presumed that intraorally, saliva, food ingredients, and beverages as well as physical factors may degrade and age dental

composites, which may reduce the longevity of a resin restoration. Furthermore, the polymer network swells by the penetration of water, ethanol or other solvents, which may lead to the initiation or propagation of microcracks at the interface between restoration and cavity wall and within the resin composite.

Chemical agents can be absorbed by adherent debris on to the denture resin surface. This leads to interactions with the resin material. Furthermore, the diffusion of fluid through the resin may also lead to initiation and propagation of microcracks at the interface and through the resin (Lee *et al.*, 1995). This action can further enhance the migration of material within the system. The processes could create a path and a reservoir of the ageing agents for further penetration into the materials and would result in their accelerated degradation. (Wu and McKinney, 1982; McKinney and Wu, 1985).

Composites, conventional and resin-modified glass ionomer cements are all susceptible to various modes of chemical degradation *in vitro*. Reduction in wear resistance, hardness, fracture toughness and flexural strength had been reported after exposure to various food-simulating liquids (Wu and McKinney, 1982; McKinney and Wu, 1985; Kao, 1989; Yap *et al.*, 2000)

2.5.5 Solvent effect in denture soft lining materials

Several authors have investigated the influence of storage media on changes in viscoelasticity (Murata *et al.*, 1996; Jepson *et al.*, 2000). In 1996, Murata *et al.* examined the effect of immersion solutions (10% acetone/ 90% water, 20% acetone/80% water, hexane, and distilled water as a control solution) on the viscoelasticity of four temporary denture soft lining materials (Coe Comfort™, Coe Soft™, GC Soft-Liner™, Visco-gel). They used a modified penetrometer to record creep strain and strain during recovery. Testing was performed at 2 and 24 hours and then at 2, 4, 7 14, 21, and 28 days after sample preparation. They got a significantly greater reduction (at least 50%) in compliance for hexane immersion than for any other solvent.

Changes in the viscoelasticity of temporary denture soft lining materials over time in the mouth are characterised by a more rapid and increased reduction in compliance than is

observed following *in vitro* immersion in water, isotonic saline, artificial saliva or denture cleaners (Graham *et al.*, 1990; Jepson *et al.*, 1993b). An accelerated rate of loss of ethanol and plasticiser as a result of solvent action *in vivo* is a possible explanation of the differences in clinical and laboratory changes in compliance. Hence, Murata *et al.* (1996) suggested hexane or similar solvents may form the basis of more clinically relevant immersion regimes. However, hexane is an aggressive solvent to simulate clinical conditions, and it can not be used in food and drinks.

Jepson *et al.* (2000) also examined the effect of immersion in dietary simulating solvents on the viscoelasticity of temporary denture soft lining materials. Four temporary denture soft lining materials were immersed in distilled water and four dietary simulating solvents (8% ethanol, 50% ethanol, corn oil, and heptane). The solvents were prepared in accordance with the FDA recommendation for the simulation of indirect food additives. Measurements were made at certain aging intervals (at 2, 24 hours, 2, 4, 7 days, and 4 weeks). They found distilled water, 8% ethanol, and 50% ethanol did not simulate clinical changes in compliance. They suspected the more profound overall reductions in compliance seen with heptane and corn oil immersion indicated a significant solvent influence. The mechanism of change in viscoelasticity had been the result of the combined effects of loss of ethanol, water absorption, and loss of plasticiser (Ellis *et al.*, 1979; Jones *et al.*, 1986, 1988; Wilson, 1992; Murata *et al.*, 1996). Early reductions were greater for materials with higher ethanol content and with immersants with a more powerful solvent action. Later changes were associated with an increasing influence of solvent type, were indicative of plasticiser loss and probably reflect the solvent effect.

2.5.6 Medium chain triglycerides, fats, nutrition and diet of denture patients

There are many types of fats and oils. Basically, they are divided into three major classes: saturated, mono-unsaturated and poly-unsaturated.

Saturated fats are the most chemically stable, and can be stored for a long time at room temperature without becoming oxidised. However, some saturated fats have been strongly linked to elevated cholesterol and to cardio-vascular disease. These saturated fats

cause the body to produce excess LDL (low density lipoprotein) cholesterol, which then oxidises and builds up on the inner surface of the human circulatory system (Jerry, 2002). Not all saturated fats are bad. Only two of the saturated fats (C_{14} and C_{16}) are identified in medical problems as being culprits in cardiovascular disease (Jerry, 2002). The C_{14} and C_{16} fats are the saturated fats most common in foods. These fats contribute to obesity as well as to elevated cholesterol levels.

Poly-unsaturated fats are the least stable and can easily become oxidised at room temperature. The chemical instability of poly-unsaturated fats is believed to be linked to cancer in laboratory animals.

Mono-unsaturated fats are widely thought to be a good compromise between saturated and poly-unsaturated fats. Mono-unsaturated fats are more chemically stable than poly-unsaturated and better for the cardiovascular system than some saturated fats. Olive oil is high in mono-unsaturated fat. Medium chain triglyceride (MCT) oil is not easily stored by the human body as fat. The use of MCT oil leads to a slight reduction of cholesterol levels and an improvement in the HDL/LDL (good cholesterol to bad cholesterol) ratio. MCT oil is available from any pharmacy without a prescription in USA for use by those who have problems digesting and metabolizing ordinary fats (Jerry, 2002).

MCT oil is usually derived from coconut oil. Caprylic acid, an 8-carbon saturated fatty acid, is found in coconut oil and has been used for quite some time in fighting *Candida* yeast infections (Crook, 1986). Beside caprylic acid, two other medium chain fatty acids found in coconut oil have been found to kill *C. albicans*. Bergsson *et al.* (2001) showed capric acid, a 10-carbon saturated fatty acid, causes the fastest and most effective killing of all three strains of *C. albicans* tested, leaving the cytoplasm disorganized and shrunken because of a disrupted or disintegrated plasma membrane. Lauric acid, a 12-carbon saturated fatty acid, was the most active at lower concentrations and after a longer incubation time. This study showed great promise that all the medium chain fatty acids in coconut oil work together to kill *C. albicans* (Bergsson *et al.*, 2001).

Nutrition and diet are important factors with all edentulous patients, but particularly with geriatric persons. Many geriatric patients are undergoing a decline in their mental faculties, people become less active, and time means nothing to them. As a result, they may eat only one meal a day, and symptoms of dietary deficiencies may develop.

Decline in sensibility to taste can result in appetite loss. Loss of appetite can result in malnutrition that contributes to chronic physical disorders, deteriorating in nature. Obesity can result from an excessive intake of refined carbohydrates. This excessive intake may be caused by emotional disturbances, metabolic disorders, and/or atrophy of the taste buds. The relation of obesity to cardiac problems is well documented. The use of drugs to decrease appetite is not without danger. The action of these drugs on the central nervous system causes nervousness and also elevates blood pressure. Thus the need for geriatric people to control obesity and also give consideration to nutrition becomes a very important issue in their life.

2.6 Denture-related stomatitis and denture soft lining materials

2.6.1 Denture-related stomatitis

Denture-related stomatitis, a term used to describe pathologic changes (erythematous and edematous) found in the denture bearing mucosa under dentures, is commonly associated with angular chelitis and glossitis (Budtz-Jørgensen, 1974), is usually an expression of oral candidosis and is characterized by inflamed mucosa, particularly under the upper denture. Patients may complain of a burning sensation, discomfort, or bad taste, but in the majority of cases they are unaware of the problem. It usually affects elderly denture wearers.

2.6.2 Diagnosis of denture-related stomatitis

In 1962, Newton identified three distinct classes of denture-related stomatitis.

These classifications are described as follows:

- Type I: localized simple inflammation or pinpoint hyperemia.
- Type II: an erythematous or generalized simple type presenting as more diffuse erythema involving a part of or the entire denture-covered mucosa.

- Type III: a granular or papillary type commonly involving the central part of the hard palate and alveolar ridge.

According to current understanding, the causative factors (Samaranayake *et al.*, 2002) are:

- Fungal infection (*Candida* species)
- Ill-fitting denture causing local trauma
- Poor oral/denture hygiene.
- Hypersensitivity to denture base materials.
- Immune defects (e.g., HIV infection, AIDS)
- Xerostomia due to irradiation, drug therapy, Sjögren's syndrome
- Physiologic (e.g., old age, infancy, pregnancy)
- Malnutrition and poor diet (e.g., high-carbohydrate diet, iron, folate, and vitamin B_{12} deficiencies)
- Antibiotics (particularly broad-spectrum antibiotics)

2.6.3 Candida-associated denture-related stomatitis

C. albicans and other *Candida* species are normally present in small numbers in the oral cavity, lower gastrointestinal tract, and female genital tract. They are frequently encountered harmless commensal yeasts (or fungus), and constitute a part of the normal human microbial flora. It is a harmless commensal organism in healthy people because it is kept in check by beneficial microorganisms, but *C. albicans* is also an opportunist pathogen and can be involved in several types of infection. In the mouth it can cause the condition known as Candida-associated denture stomatitis, and is also involved in angular chelitis, median rhomboid glossitis, and linear gingival erythema etc (Samaranayake *et al.*, 2002). Occasionally, *C. albicans* is responsible for serious, life threatening systemic conditions.

Davenport (1970) and Nikawa *et al.* (1992) have reported that the main reservoirs of *C. albicans* and related species are the fitting surface of the denture and denture soft lining materials. They are easily colonised by these organisms. *Candida* associated denture-related stomatitis is observed in approximately 11% to 67% of otherwise healthy denture

wearers (Arendorf and Walker, 1987). In fact, Nikawa *et al.* (1998) have pointed out that the continuous swallowing or aspiration of microorganisms from denture plaque expose patients, particularly the immunologic compromised host or medicated elderly, under certain circumstances to opportunistic pathogens which can invade human tissues, causing severe life-threatening infections. Hence, how to inhibit or reduce the adherence, growth, and colonisation of *C. albicans* can be an important issue in clinical practice.

2.6.4 *Candida albicans* related to denture soft lining materials

In previous studies of *C. albicans* related to denture soft lining materials, the researchers focused on the inherent fungal inhibition provided by some denture soft lining materials. This may be beneficial in the treatment of denture-related stomatitis.

2.6.4.1 Inhibition of *Candida albicans* to denture soft lining materials

Gruber *et al.* (1966) prepared samples of denture soft lining materials, stored in distilled water for 72 hours and then immersed in nutrient broth in sterile petri dishes. The broth was then inoculated with pure stock cultures of *C. albicans* and incubated for five days at 25°C. Gruber et al, found that *C. albicans* grew on the surface of silicone denture soft lining materials and tissue conditioners but not on heat-cured and cold cured methacrylate-based denture soft lining materials, or heat-cured acrylic denture base resin. It was concluded that both tissue conditioners and silicone denture soft lining materials could support the growth of *C. albicans.* However, the absorption of the nutrient broth into the soft lining may be relevant.

Williamson (1968) reported a study of the effect of a range of denture soft lining materials on the growth of *C. albicans* in a medium essentially free of nutrients and in a medium to which a small quantity of saliva was added. The commercial materials were one heat-cured acrylic (Palasiv™), three cold-cured acrylic (Flexene™, Perfex™, Tempo™), one heat-cured silicone (Molloplast-B®) and one cold-cured silicone (Flexico™). Williamson mixed each denture soft lining material according to the manufacturer's instructions, placed them in sterile containers and covered them with sterile distilled water for three days. On the fourth day, the water was poured off and the

denture soft lining materials were covered with a suspension of *C. albicans* in 5ml physiological saline or 5 ml physiological saline containing 1:10 v/v saliva. Saline was selected because it lacked nutrient medium and therefore any growth of organisms which occurred on a denture soft lining material could be attributed to the material. Incubation was carried out for five days at 27°C. Williamson then took surface viable counts by making 1:100 dilutions of the media and spreading 0.1 ml on a Sabouraud's agar plate. The plates were then incubated for 48 hours and colonies of *C. albicans* counted. Williamson's study showed that counts of *C. albicans* on Flexico™, Perfex™ and Palasiv™ were no different from controls, indicating that these materials were without effect on *C. albicans.* However, Molloplast-B® was found to have an inhibitory effect on *C. albicans* in saline medium. Flexene™ and Tempo™ showed a significant reduction in *C. albicans* populations in both saline and saline/saliva media, indicating an inhibitory effect on the yeast.

Table 2.7 Denture soft lining materials investigated in Wright's study (1980b).

Material	Commercial name	Types of materials	Manufacturer
A	Flexibase™	Room-cured silicone	Flexico Ltd, UK
B	Simpa™	Room-cured	Ketterbach, Germany
C	Cardex-Stabon™	Room-cured	Cardex, Austria
D	Per-Fit™	Heat-cured	Dental Products Unlimited, USA
E	Molloplast B®	Heat-cured silicone	Kostner and Co., Germany
F	Coe-Soft™	Room-cured acrylic	Coe Laboratories Inc., USA
G	Soft Oryl™	Room-cured	The William Getz Corp., USA
H	Ardee™	Used as supplied	Reliance Dental MfG. Co., USA
I	Coe Super-soft™	Heat-cured acrylic	Coe Laboratories Inc., USA
J	Palasiv 62™	Heat-cured acrylic	Kulzer and Co., Germany
K	Soft Nobiltone™	Heat-cured	Nobilium Products Inc., USA
L	Virina™	Heat-cured	Virina Dental Products Ltd, Canada
M	Verno Soft™	Heat-cured	Verno-Benshoff Co. Inc., USA
N	Experimental	Heat-cured	R. H. Cole and Company Ltd, UK
O	Experimental	Heat-cured	A.D.I. Plastics, UK
P	Experimental	Heat-cured	Hydron Dental Products Inc., USA
Q	Experimental	Heat-cured	The Malaysian Rubber Producers'

In 1980, Wright reported the effect of denture soft lining materials on the growth of *C. albicans*. In Wright's comprehensive work, he set out a test methodology for assessing the effect of denture soft lining materials on *C. albicans* populations, assessed seventeen commercial and experimental denture soft lining materials and identified some of the active ingredients and their efficacy in inhibiting Candidal growth. The tested materials are listed Table 2.7. The materials listed in the table marked A-E are silicone-based

denture soft lining materials; materials F-H are tissue conditioners; materials I-P are methacrylate-based denture soft lining materials; material N incorporates a polymerisable plasticiser whilst material P has no constituent plasticiser, but incorporates poly(hydroxyethylmethacrylate) which absorbs large amounts of water, in effect the water plasticises this material. Finally, material Q is a natural rubber incorporating a zinc dimethyl dithiocarbamate-sulphur curing system.

The *C. albicans* used in these tests was incubated on a blood agar plate for 24 hours. A few colonies were then transferred to 20ml of nutrient broth and incubated for a further 24 hours. This culture was then centrifuged and the yeasts re-suspended in 5ml of nutrient broth. Next, Diagnostic Sensitivity Test (DST) agar was melted and poured into sterile petri dishes. These plates were then inoculated with the broth culture by flooding the surfaces and pouring off any excess. These plates were then allowed to dry in the inverted position in an incubator at 37°C for 30 minutes. To each plate, Wright added three test disks of denture soft lining material and one filter paper disk containing 100 units of Nystatin as a control. Each denture soft lining material was tested on two plates, using six test disks and two controls. With the test and control disks in place, the plates were incubated for a further 24 hours at 37°C. Those denture soft lining materials that inhibited growth of *C. albicans* showed a clear kill zone around the circumference of the disk. Measurements of kill-zone radii were taken using dividers with strong reflected light. To enable the comparison of tests on one plate with those on another, the degree of inhibition was calculated relative to that caused by the Nystatin control disks. Wright found that four of the denture soft lining materials exhibited an inhibitory effect on *C. albicans*. Most effective were Simpa™ and the natural rubber-based experimental material. Flexibase™ was also found to inhibit *C. albicans*, but only was half as effective as Simpa™. Molloplast-B® also showed evidence of inhibition, although this was deemed to be a slight effect as the kill zone was too small to measure.

Wright (1980b) also analysed the ingredients of those denture soft lining materials proved to inhibit *C. albicans*. To assess the inhibitory effect of any liquid components, sterile disks of filter paper were immersed in the liquid and, once excess liquid was shaken off,

the disks were placed on to seeded DST agar plates. Solid constituents were assessed by cutting out small pieces of the material and placing them onto seeded DST agar plates. Nystatin control disks were once again placed on each plate to enable comparison between plates. Simpa™ and Flexibase™ are both room temperature vulcanizing silicone rubbers. The basic silicone polymer is α-ω-dihydroxy end-blocked PDMS which is mixed with a cross-linking agent called ethyl poly silicate and an activator, dibutyltin dilaurate. Tests on each of these constituents showed that dibutyltin dilaurate was the active inhibitory ingredient. Molloplast-B® is a heat-cured silicone-based denture soft lining materials. The exact composition is not in the public domain, although it is known that γ-methacryloxypropyl-trimethoxysilane is added to the rubber to improve adhesion to the PMMA denture base. When tested, this constituent proved to inhibit the growth of *C. albicans*. The experimental natural rubber-based lining that was found to have a nominal inhibitory effect on *C. albicans* was also tested and in this case, the catalyst, dithiocarbamate was found to be the active ingredient in inhibiting the yeast.

Wright (1980b) also investigated the relationship between the amount of dibutyltin dilaurate in Simpa™ and its inhibitory behaviour. This was achieved by preparing several samples of the denture soft lining material with differing quantities of dibutyltin dilaurate and again placing them on seeded DST agar plates with a Nystatin disk control. Wright found a linear relationship between the amount of dibutyltin dilaurate and the inhibitory effect of the samples.

Wright (1980b) designed a further test to see whether the active agent, dibutyltin dilaurate, would leach out of Simpa™ in an aqueous environment. If dibutyltin dilaurate leached in large amounts, it would suggest that while Simpa™ might inhibit Candidal growth for a period after being applied to a denture, it would soon lose this capacity for inhibition. To find out, Wright placed disks of Simpa™ in sterile distilled water at 37°C for periods ranging from ten minutes to seven weeks. These disks were then placed on seeded DST agar plates and kill zones of *C. albicans* measured as in the previous experiments. The results showed a marked decrease in *C. albicans* inhibition over a five week period, as would be expected. While Wright's extensive investigation identified

both the denture soft lining materials and their active constituents that inhibited *C. albicans*, these results cannot be used to determine the best denture soft lining material for use in a clinical application, since water absorption, solubility and surface characteristics will also influence the growth of *C. albicans* both in and on the denture soft lining material.

In 1998, Wright *et al.* proposed an alternative method for assessing the effect of denture soft lining materials on the growth of yeasts. Wright *et al.* looked at the effect of two commercial denture soft lining materials, Coe Supersoft™, a conventional methacrylate-based denture soft lining material (Coe Labs, Inc., Chicago) and Novus™, a poly(fluoro alkoxy) phosphazine elastomer, and three experimental soft lining materials. Wright *et al.* (1998) assessed the growth on soft linings of three key *Candida* species (*C. albicans*, *C. tropicalis* and *Issatchenkia orientalis*), each of which have previously been isolated from denture soft lining materials. This was achieved by inoculating blood agar plates with yeast suspensions and placing a strip of denture soft lining material on each plate. The plates were then incubated at 37°C and examined at 24 hours and one week for kill zones. In addition to kill zones, Wright et al examined both the area of agar under the strip and also the underside of each strip. They found that only the experimental material RTV produced zones of inhibition for all *Candida* species. Again, in the case of RTV, the inhibitory effect was attributed to a small amount of dibutlytin dilaurate which had been added as a catalyst.

In addition to studies on the inhibition of yeast to denture soft lining materials, some research groups have studied the effect of denture soft lining materials on the adherence of growth of *C. albicans*.

2.6.4.2 Adherence of *Candida albicans* to denture soft lining materials

In 1992, Nikawa *et al.* reported an in vitro evaluation of *Candida albicans* adherence to a variety of commercial denture soft lining materials. The commercial materials tested are reproduced in Table 2.8. They placed samples on culture plates and added yeast suspension. The plates were then centrifuged to bring the *Candida* organisms into contact

with the denture soft lining materials and then incubated for ten minutes at 37°C after which, non-adherent yeasts were washed off with distilled water. The samples were then dried in a desiccator overnight at room temperature and the yeast adherence estimated using a BCA (bicinchoninic acid) protein assay reagent method.

Table 2.8 Soft linings assessed for adherence of *Candida albicans* by Nikawa *et al.*, 1992.

Material	Types of DSLM	Manufacturer
Coe Comfort™	Tissue conditioner	Coe Inc., USA
Coe Soft™	Tissue conditioner	Coe Inc., USA
Fit Softer™	Tissue conditioner	Sankin Co., Japan.
Fitt™	Tissue conditioner	Kerr/Sybron, USA
GC Soft Liner™	Tissue conditioner	GC Corp., Japan.
Hydrocast™	Tissue conditioner	Kay-See Co., USA.
Visco-gel	Tissue conditioner	De Trey/Dentsply, UK

Nikawa *et al.* (1992) investigated the adherence of *C. albicans* to the bare and saliva-covered denture soft lining materials. Adherence of the yeast to bare surface of denture soft lining materials, in decreasing order was: Coe-Comfort™, Coe Soft™, GC Soft Liner™, Hydrocast™, Visco-gel, Fit Softer™ and Fitt™. This order of adherence agreed with the relative hydrophobic properties of the substrates as determined by contact angle measurements as reported in an earlier part of the same paper. The adherence of *Candida* to saliva-coated soft linings was far reduced in every case except for the Fitt™. However, between different saliva-coated denture soft lining materials, there were no significant differences in yeast adherence. These results suggest that the adherence of *C. albicans* to saliva-coated denture soft lining materials is governed by factors other than hydrophobicity. Nikawa *et al.* (1992) thought that for *C. albicans* adherence to tissue conditioners, the nature of salivary proteins bound to denture soft lining materials by pellicle may play a more important role than the surface properties of tissue conditioners.

Waters and his colleague (1997) assessed the ability of *C. albicans* to adhere to two room-temperature cured experimental silicone rubbers and compared the results with commercially available Molloplast-B® silicone-based denture soft lining material and Trevalon™ heat-cured methacrylate-based denture base resin. The samples were prepared in a stainless-steel mould with highly polished surfaces to give reproducible results. *C. albicans* was incubated in Sabouraud's broth, and Candidal growth was harvested after 24 hours by centrifugation. The samples were deposited in 20 ml yeast suspension in

sterile petri dishes. The materials were incubated for one hour at room temperature. Then the materials were washed twice by gentle agitation in phosphate buffered saline solution for one minute. After the materials were dried, adherent yeast cells were fixed and stained.

Waters *et al.* (1997) investigated the adherence of *C. albicans* to the bare and saliva-covered denture soft lining materials. Adherence of the yeast to bare surface of denture soft lining materials, in increasing order was: two experimental silicone rubbers, Trevalon™ and Molloplast-B®. The adherence of *C. albicans* to saliva-coated soft linings was also reduced in every case, and to the experimental rubbers was significantly less than Trevalon™ and Molloplast-B®. They also thought the nature of the salivary proteins bound to the denture surfaces by pellicle clearly played an important role in the level of Candidal adhesion. However, *Candida*-associated denture-related stomatitis is also known as a common problem among patients with xerostomia due to irradiation, drug therapy, Sjögren's syndrome and older people with malnutrition, in which salivary flow is absent or minimal.

2.6.5 Summary

It has been established that the use of denture soft lining materials provide a useful adjunct to the treatment of edentulous and partial edentulous patients. However, the materials have a number of deficiencies which allow degradation and possible fungal infection. These problems need further investigation prior to the development of new materials, modification of existing materials or surface treatment which might improve their clinical performance and prevent degradation of the materials.

CHAPTER THREE

AIMS AND OBJECTIVES

The key aim of this research was to investigate the possible causes of intra-oral degradation of long-term denture soft lining materials. The following methods will be used: water and fluid absorption and desorption via a fixed volume of fluid unchanged for the duration of the experiment and via a fixed volume of fluid changed at every measurement point.

The effect of water and fluid absorption characteristics will be evaluated by assessment of surface roughness, hardness and wettability behaviour.

Supporting investigations will include particle size analysis for polymer powder, analysis of substances released from materials after fluid immersion, and adherence of *Candida albicans* to materials following fluid immersion.

The main hypothesis is that immersion of denture soft lining materials in defined food-simulating liquids causes degradation similar to that seen during intra-oral use. The subsidiary hypotheses are that changing the immersion fluid on a frequent basis affects the results of fluid immersion, and fluid immersion has no effect on the surface roughness of the material, the softness of the material, the wettability of the material, and the adherence of *Candida albicans*.

CHAPTER FOUR

MATERIALS AND METHODS

4.1 Materials

Four commercial denture soft lining materials and one experimental elastomer were chosen on the basis of their different chemical compositions. Table 4.1 lists the abbreviation code, manufacturers and presentation used to describe each denture soft lining material. Table 4.2 shows each denture soft lining material, and their composition according to the manufacturer.

Table 4.1 Denture soft lining materials investigated

Soft Lining Material	Code	Manufacturers	Presentation
Vertex™Soft (heat-cured acrylic resin)	VT	Dentimex BV, Holland	Powder and liquid
EverSoft® (methyl methacrylate-free acrylic resin)	ES	Myerson, Austenal Ltd, UK	Powder, liquid and sealer
Molloplast B® (heat-cured silicone elastomer)	MB	Karl Huber GmbH & Co. Germany	Single component paste
Ufi Gel SC (self-cured silicone elastomer)	UG	Voco GmbH, Germany	Cartridges (auto-mix) and glazer
Bromo butyl butyl elastomer (heat-cured experimental elastomer)	BE	QMUL, UK	Elastomer and liquid

Table 4.2 Denture soft lining materials composition

Code	Powder (paste, base, elastomer)	Liquid
VT	polyethyl methacrylate	acetyl tributyl citrate (plasticizer, < 80%) methyl methacrylate (> 15%) crosslinker (<5%)
ES	polyethyl methacrylate	di-n-butyl phthalate (plasticizer) (60-90%) ethyl acetate (5-15%) ethyl alcohol (1-10%)
MB	α-ω-dihydroxy terminated poly(dimethyl siloxane)	
UG	vinyl dimethyl polysiloxane, hydrogen poly siloxane, silicone dioxide, fumed silica	
BE	bromo butyl elastomer	butyl methacrylate

Code	Initiator (catalyst)	Cross-linking agent	Sealer (glaze)
VT	benzoyl peroxide		
ES			methyl ethyl ketone
MB	benzoyl peroxide		
UG	vinyl dimethyl polysiloxane, silicone dioxide		the same as base and catalyst
BE	1% lauryl peroxide	1% ethylene glycol dimethacrylate	

4.2 Specimen Manufacture

4.2.1 Mould for fabrication of specimen (Fig 4.1)

Auto-mixed polyether impression material was used to produce a template for the specimen sheets, 1mm in thickness, by placing the mixed impression material in the centre of a mould comprising a 1 mm spacer which was sandwiched between two metal plates. The assembly was then placed in a hand operated hydraulic press and pressure applied slowly to expel any trapped air and excess material. On setting, the 1 mm thick sheet of polyether material was removed from the mould. Disc samples were cut from the sheet, 20 mm in diameter and 1 mm thick, using a cork borer. These discs were then invested in stone using the conventional dental flasking technique. Once the stone had set, the flask was separated and the rubber discs removed. The mould produced could be used for specimen production of the test materials.

4.2.2 Preparation of soft acrylic denture lining materials (Fig 4.1)

Vertex™Soft and EverSoft® were both supplied as a two-component system, a polymer powder and in the case of Vertex™Soft a liquid contains monomer, plasticiser and cross-linking agent. However, EverSoft® liquid was a mixture of di-n-butyl phthalate, ethyl acetate and ethyl alcohol. A sealer (a methyl ethyl ketone) was also provided with EverSoft®. The components were mixed in the ratios recommended by manufacturers.

The mixing time for Vertex™Soft was 60 seconds at ambient temperature. The mixing ratio of powder to liquid recommended by manufacturers, 2:1 by weight was used. The mixing ratio for EverSoft® was recommended at 2.5:1 by weight. The powder/liquid mixture was packed into the flask at the dough consistency which was then processed. This was achieved by transferring the soft acrylic materials directly to the mould at the dough stage. A polyethylene sheet was used as a separating medium placed over the soft acrylic materials, and the flask was reassembled. The flask assembly was then placed into a hand operated hydraulic press. The press was closed by slowly applying pressure during the trial closure to expel the excess soft acrylic materials. The separator sheet allowed easy separation of the flask halves during the trial closure procedures. Using a rounded

instrument, the flash was carefully teased away from the mould. A fresh polyethylene sheet was placed between the major portions of the flask, and the flask closed. The flask assembly was once again loaded in the press. Another trial closure was made. Trial closures were repeated until no flash was observed. When flash was no longer apparent, definitive closure of the mould was accomplished. During the final closure process, no polyethylene sheet was interposed between the moulds. Again, pressure was applied incrementally. The flasks then were transferred to a flask carrier. The flask carrier maintained pressure on the flask during the processing cycle. The dental flasks were then placed in water bath (Multi-cure Derotor, Quale Dental, Worthing, UK), to be heated according to their respective manufacturer instruction.

For Vertex™Soft the manufacturer recommended a curing time of 3 hours at 70°C and then 30 minutes at 100°C (fast curing method), which was reported to be an adequate time for polymerisation. However, the manufacturers of EverSoft® recommended placement in the 37±1°C water bath for one hour, and then in boiling water (100°C) for 15 minutes.

After the materials had been through the appropriate curing heating cycle, the flask was removed from the water bath and allowed to cool down to room temperature, standing in air. After cooling, the specimens were carefully removed from the moulds. Specimens of Vertex™Soft were randomly divided into seven groups of six specimens and five groups of three specimens. Specimens were then preconditioned by storing in a desiccator at 37±1°C.

At this point, the sealer recommended by EverSoft® was applied (to EverSoft® only). The specimen surface was dried by using air to remove all surface moisture. A generous coat of sealer was applied over the specimen's totally dry surface and air dried for over 2 minutes. The procedure was repeated by adding a second and third coating. The specimens were randomly divided into seven groups of six specimens, and preconditioned by storing in a desiccator at 37±1°C.

4.2.3 Preparation of silicone rubber denture soft lining materials (Fig 4.1)

Molloplast-B® is a one-paste system and therefore requires no mixing. It was pressed into the mould directly using dental instruments. As before, a polyethylene sheet acted as a separator during the trial closure. Trial closures were carried out, as described previously until no excess paste was observed. When excess paste was no longer apparent, definitive packing of the mould was accomplished. During this final closure process, no polyethylene sheet was interposed between the moulds, and pressure was applied incrementally. The flasks were transferred to a flask carrier. The flask carrier maintained pressure on the flask during the processing cycle. The dental flasks were then placed in a water bath (Multi-cure Derotor, Quale Dental, Worthing, UK), to be heated according to the manufacturer's instructions.

For Molloplast-B® the manufacturer recommended a curing cycle in which the flask was placed in the cold water bath and heated gradually to 100°C. It was maintained at this temperature for half an hour. After that, the flask was removed from the water bath and allowed to cool down to room temperature, standing in air. After cooling, the specimens of Molloplast-B® were carefully removed from the moulds, randomly divided into seven groups of six specimens and five groups of three specimens. Specimens were then preconditioned by storing in a desiccator at 37±1°C. Ufi Gel SC is a chair-side silicone rubber denture soft lining material. This means it required no additional heat activation. Unlike Molloplast-B®, Ufi Gel SC is a two-paste system. The two pastes were mixed together in a 1:1 ratio by an automixer syringe. The material was syringed into the mould and then followed the trial packing procedures described above. The working time was stated by the manufacturer to be 5 minutes. For curing the moulds were flasked and placed in the pressure pot at 40-45°C for 15 minutes. It was then removed from the pressure pot and allowed to slowly cool down for 20 minutes. After cooling at room temperature, the cured specimens of Ufi Gel SC were then carefully removed from the moulds. At this point, the glazing procedure recommended by the Ufi Gel SC manufacturer was used. The specimen's surface was dried by using air to remove all surface moisture. Equal numbers of drops of the glazing base and catalyst were mixed with a brush homogeneously in a plastic mixing container. Sufficient material was mixed

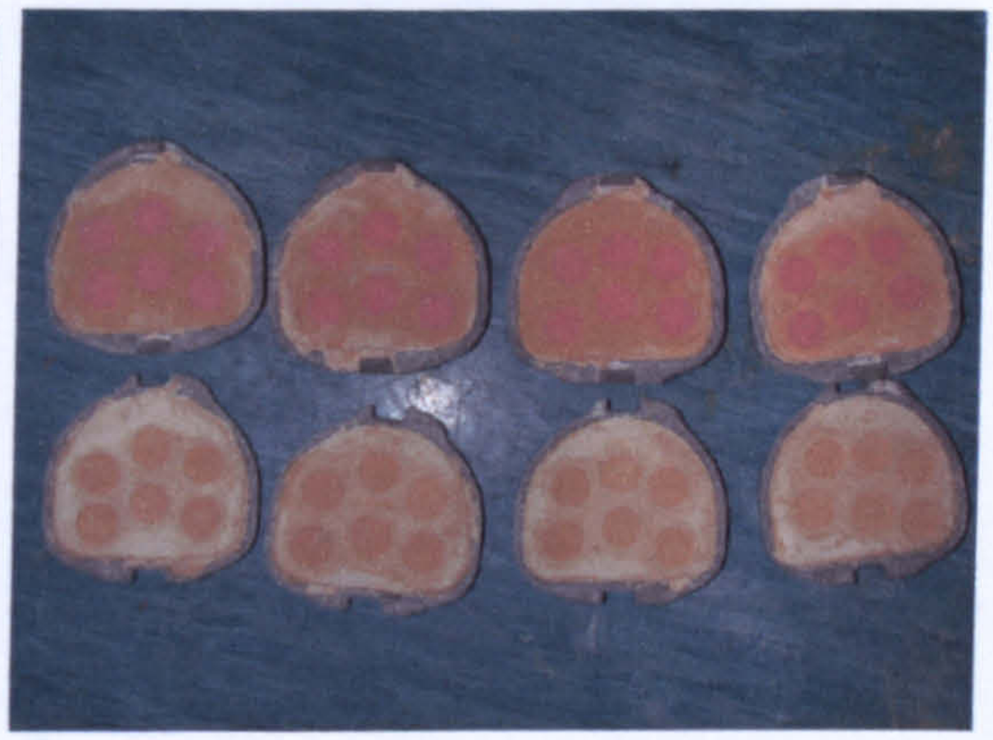
in each case to coat six specimens within the working time (two minutes) of the glazing. After setting (ten minutes), the specimens were also randomly divided into seven groups of six specimens and five groups of three specimens. Specimens were then preconditioned by storing in a desiccator at 37±1°C.

4.2.4 Preparation of bromo-butyl butyl elastomer (Fig 4.1)

The elastomer used is listed in Table 4.1 and was supplied by Bayer AG. Table 4.2 above also shows the details of this material supplied by the manufacturer. The butyl elastomer was used with a monomer mixture, consisting of *n*-butyl methacrylate (*n*-BMA), 1% lauryl peroxide (LP) (wt/wt)(as initiator) and 1% ethyl glycol dimethacrylate (EGDMA) (wt/vol) (as cross-linking agent) . The butyl elastomer was cut into small sections (approximately 10 mm^3), using a sharp blade. 100 gram of elastomer was mixed with 100 ml of monomer liquid. This mixture was left in a glass jars to swell for a period of two days in a refrigerator at 4±1°C and was then milled on a roller mill for 5-10 minutes to ensure homogeneity at least 48 hours prior to moulding and curing.

Moulding was undertaken according to general sample preparation where the gels were packed into the flask. Trial closures were carried out as described before. Trial closures were repeated until no flash was observed. When flash was no longer apparent, definitive closure of the mould was accomplished. During the final closure process, no polyethylene sheet was interposed between the moulds. Again, pressure was applied incrementally. The flask was transferred to a flask carrier. The flask carrier maintained pressure on the flask during the processing cycle. The dental flasks were then placed in a water bath (Multi-cure Derotor, Quale Dental, Worthing, UK), and the following curing cycle used. An initial 2 hour period at 74°C followed by 30 minutes at 100°C (fast curing method), which was determined to be an adequate time for appropriate polymerisation. After the BBBE had cured, the flasks were removed from the water bath and allowed to cool to room temperature, standing in air. After cooling, the specimens of BE were then carefully removed from the moulds, randomly divided into seven groups of six specimens and five groups of three specimens. Specimens were also then preconditioned by storing in a desiccator at 37±1°C.

A

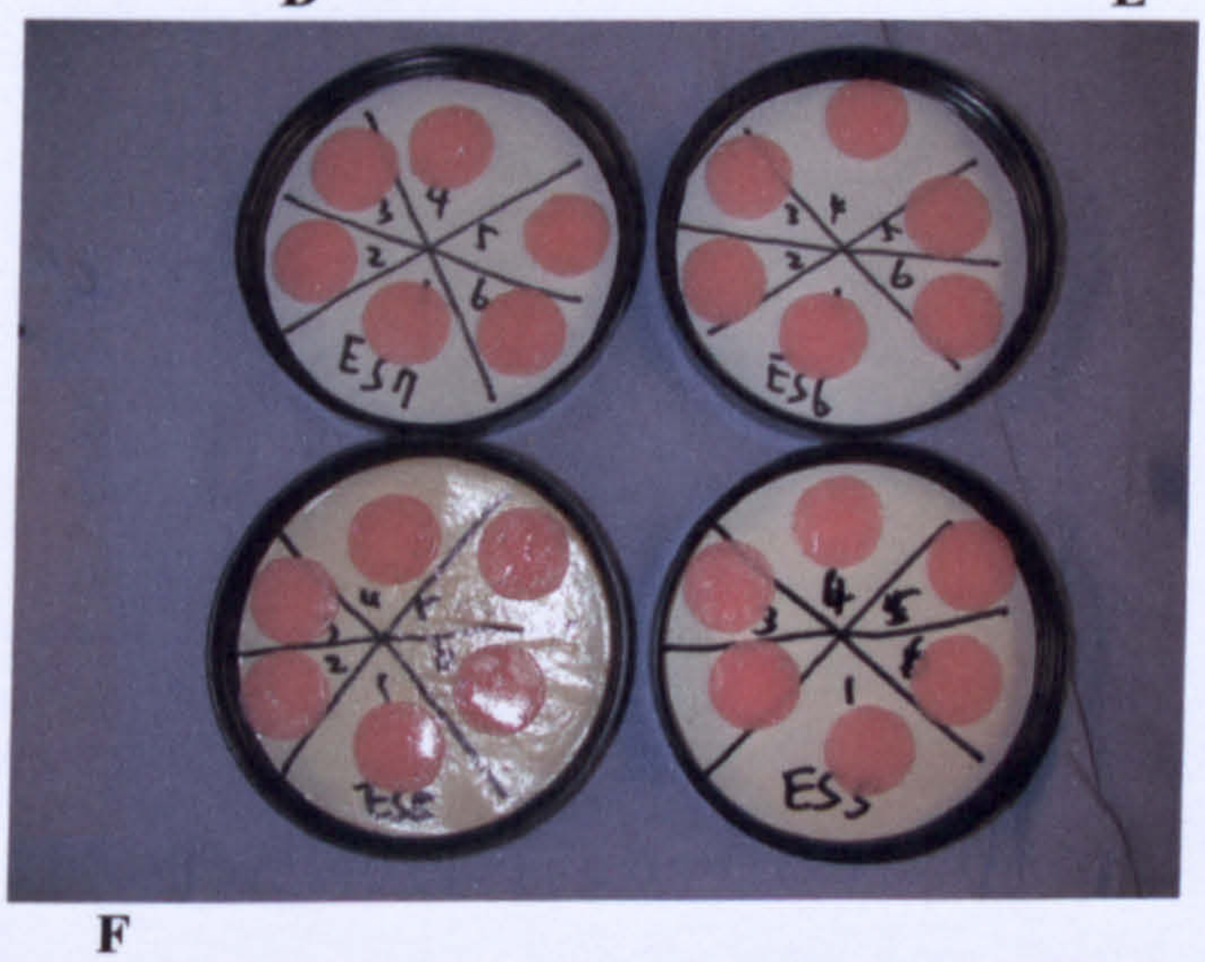


B

C

D

E



F

Figure 4.1 Mould and procedures used to form specimens. **A**, A polyethylene sheet was used as a separating medium placed over the soft acrylic materials. **B**, Trial closures were repeated until no flash was observed. **C**, The final closure process, no polyethylene sheet was interposed between the moulds. Again, pressure was applied incrementally. **D**, The flask carrier maintained pressure on the flask during the processing cycle. **E**, The dental flasks were then placed in a water bath, to be heated according to their respective manufacturer instruction. **F**, The specimens were then randomly divided into groups of six specimens.

4.3 Physical and Structural Characterisation

4.3.1 Water and Fluid Absorption Characterisation

All specimens were processed according to the manufacturers' directions. A total of 42 specimens were constructed for each denture soft lining material. The specimens were then randomly divided into seven groups of six specimens. Specimens were preconditioned after manufacture by storing in a desiccator at 37±1°C. The specimens were removed from the desiccator, immediately weighed and then were weighed at regular intervals up to one year. All readings were taken to an accuracy of ± 0.0002g on an AE Mettler electronic balance (Metler-Toledo Ltd, Leicester, UK). This initial weight was noted W_0. After weighing, each specimen was immediately transferred to a wide mouth, amber, screw topped glass jar containing 50 ml of food simulating liquids. The immersing liquids selected were distilled water (DW), artificial saliva (AS) (composition shown in Table 4.3) (Fusayama *et al.*, 1963), 3% aqueous acetic acid (3AA) (EC Food Contact Legislation, 2000), 10% ethanol (10E), 50% ethanol (50E), coconut oil (CO) and HB307 (HB) (FDA, 2002) (Table 4.4 and Table 4.5). Each glass jar was then stored in an incubator (LABHEAT Model RLCH0400, Boro Labs Ltd, Berkshire, UK) at 37±1°C. Each specimen was removed at predetermined time intervals (Table 4.6) using tweezers and carefully blotted to remove excess surface liquid using filter paper prior to weighing. The weights were then recorded. Initial intervals between weighing were short but subsequently were increased. The fluid was unchanged for the duration of the experiment but was topped up after each measurement to maintain a fixed volume. At two months, 25 ml of fresh 50 per cent ethanol solution was added to maintain a fixed volume, following the evaporation of ethanol in the incubator and the process of measurement.

Table 4.3 Composition of artificial saliva (Fusayama *et al.*, 1963).

Component	Quantity (g/1000mL)	MW	Manufacturers
Urea [$CO(NH_2)_2$]	1.0	60.06	Sigma Chemical Co.
Calcium Chloride ($CaCl_2.2H_2O$)	0.6	147.0	Sigma Chemical Co.
Sodium Phosphate (Na_2HPO_4)	0.6	142.0	Sigma Chemical Co.
Sodium Chloride (NaCl)	0.4	58.44	Sigma Chemical Co.
Potassium Chloride (KCl)	0.4	74.55	Sigma Chemical Co.
Magnesium Pyrophosphate ($Mg_2P_2O_7$)	0.0016	222.57	Aldrich Chemical Co.
Sodium Sulfide (Na_2S)	0.0016	78.04	Aldrich Chemical Co.

Table 4.4 Composition of coconut oil (http://www.coconutoil-online.com) and HB307 (NATEC, 2000) by percentage of composition.

Coconut oil Component	Percentage composition
Lauric acid (C_{12})	47.10%
Myristic acid (C_{14})	18.00%
Palmitic acid (C_{16})	9.00%
Capric acid (C_{10})	7.50%
Stearic acid (C_{18})	3.06%
Caprylic acid (C_8)	8.86%
Traces C_{15}	0.01%
Linoleic acid $C_{18:2}$	0.76%
Oleic acid $C_{18:1}$	4.44%
Arachidic (C_{20})	0.05%
HB307 Component	**Percentage composition**
Lauric acid (C_{12})	52.9%
Myristic acid (C_{14})	14.6%
Capric acid (C_{10})	10.2%
Stearic acid (C_{18})	8.4%
Palmitic acid (C_{16})	7.1%
Caprylic acid (C_8)	6.3%
Diglyceride	0.7%
Monoglyceride	< 0.4%

Table 4.5 Food simulating liquids used in this study

Food simulating liquids	Code	Simulated food	Manufacturers
Distilled water	DW	Aqueous foods (control)	Queen Mary, University of London
Artificial saliva	AS	Saliva	Fusuyama formulation
3% Acetic acid	3AA	Aqueous & acidic foods	BDH Chemical Co.
10% Ethanol	10E	Aqueous & low-alcoholic foods	BDH Chemical Co.
50% Ethanol	50E	High-alcoholic foods	BDH Chemical Co.
Coconut Oil	CO	Fatty foods	Coconut oil from Cocos nucifera, C1758, Sigma Chemical Co. USA.
HB307	HB	Fatty foods	NATEC GmbH, Hamburg, Germany

Simplified Guide to EC Food Contact Legislation(2000); U.S. Food and Drug Administration (FDA). (2002)

Table 4.6 Measurement regime for water and fluid uptake studies. (solution unchanged)

Week no.	Period	Measurements taken at...
1	Day 1	0, 30, 60, 120, 240, 360 minutes, 24 hours
	Day 2	48 hours
	Day 3	72 hours
	Day 7	168 hours
2	Day 14	336 hours
3	Day 21	504 hours
4	Day 28	672 hours
8	Day 56	1342 hours
16	Day 102	2684 hours
26	Day 182	4368 hours
52	Day 364	8736 hours

After a period of 52 weeks, specimens were removed from solution, weighed and then desorbed in an incubator (Gallenkamp Durastat Type 3, LTE Scientific Ltd, Oldham, UK) at 37±1°C. Specimens were weighed at regular intervals until a minimum weight was reached (W_d). Percentage weight change and percentage solubility were calculated as a percentage of the initial weight. Real percentage uptake was calculated as the sum of percentage weight change and percentage solubility, and desorption diffusion coefficients by the application of solutions of Fick's equations.

$$\% \text{ Upake} = \left(\frac{W_t - W_0}{W_0} \right) \text{ X } 100 \qquad (4.1)$$

$$\% \text{ Solubility} = \left(\frac{W_0 - W_d}{W_0} \right) \text{ X } 100 \qquad (4.2)$$

$$\text{Real } \% \text{ Uptake} = \% \text{ Uptake} + \% \text{ Solubility} \qquad (4.3)$$

Where W_0 = initial weight, W_t = weight at time t and W_d = final minimum desorbed weight. The diffusion coefficient was measured to determine the rate of passage of fluid through the material. The diffusion coefficient was calculated from the slope of the linear parts of the plot (Crank, 1975);

$$\frac{M_t}{M_\infty} = 2\left(\frac{Dt}{\pi l^2}\right)^{1/2} \quad (4.4)$$

Where M_t = weight at time t, M_∞ = weight at equilibrium, $2l$ = specimen thickness and D = diffusion coefficient. The equation is appropriate for the early stages of diffusion where $M_t/M_\infty \leq 0.5$. M_t/M_∞ should be linear to $t^{1/2}$. The slope (S) of the linear plot is given by;

$$S = 2\left(\frac{D}{\pi l^2}\right)^{1/2} \quad (4.5)$$

And rearranged to give the diffusion coefficient;

$$D = \frac{\left(S^2 \pi 4 l^2\right)}{16} \quad (4.6)$$

The initial water uptake/solubility study showed in certain cases substantial amounts of material were released. To decide whether the concentration of solute in the immersing solution was influencing release of solute, a further experiment was carried out when the immersing solution was changed at regular intervals (Table 4.7). Immersing solutions evaluated were DW, AS, 3AA, 10E and 50E.

Table 4.7 Measurement regime for water and fluid uptake studies. (changed solution)

Week no.	Period	Measurements taken at...
1	Day 1	0, 60 (C), 360 (C) minutes, 24 (C) hours
	Day 2	48 (C) hours
	Day 3	72 (C)hours
	Day 7	168 (C) hours, and change solution weekly from day 7.
2	Day 14	336 (C) hours
3	Day 21	504 (C) hours
4	Day 28	672 (C) hours
8	Day 56	1342 (C) hours
12	Day 84	2016 (C) hours
16	Day 102	2684 (C) hours
20	Day 140	3360 (C) hours
26	Day 182	4368 (C) hours

(C): changed immersing solution

All specimens were processed according to the manufacturers' directions. A total of 15 specimens were constructed for each soft lining material. The specimens were then randomly divided into five groups of three specimens. Specimens were preconditioned in

a desiccator at 37±1°C, weighed at regular intervals up to six months. This initial weight was noted W_0. After weighing, each specimen was immediately transferred to a wide mouth, amber, screw topped glass jar containing 50ml of food simulating liquids (Table 4.4) excluding oils.

The procedures followed were similar to that in earlier experiments except that the immersing solution was changed at each time the specimen was weighed, or every seven days whichever was the sooner. After a period of 26 weeks, specimens were removed from solution, weighed and then desorbed in an incubator (Gallenkamp Durastat Type 3, LTE Scientific Ltd, Oldham, UK) at 37±1°C. Percentage weight change, percentage solubility and percentage real uptake were calculated as before.

The statistical differences between test groups were analysed by the non-parametric Mann-Whitney U test for comparing two independent samples and the Kruskal-Wallis H test for comparing three or more independent samples, using SigmaStat® Statistical software for Windows version 3.0. P value of < 0.05 was considered statistically significant.

4.3.1.1 Visual assessment

All specimens were examined visually at one month, four months and one year compared with as processed samples of Molloplast-B® so that the dimensional changes could be noted. All changes were recorded on a simple grading system of three grades, slight, moderate and marked.

4.3.2 Surface Roughness Characterisation

4.3.2.1 Preparation of replica surfaces

Once the immersion cycle had commenced, impressions of the immersed specimens were taken immediately and at the prescribed time intervals for weight measurement. Impressions of VT, ES, MB, UG, BE surfaces were made, using mid-blue, light-bodied vinyl polysiloxane impression material (Extrude™, Kerr Ltd, Peterborough, UK). These vinyl polysiloxane negative replicas were used to measure the surface roughness of

specimens of soft lining materials. After setting, the replica was carefully separated from the specimen, and stored in a covered box at room temperature until the replica was subsequently scanned by a laser profilometer.

4.3.2.2 Laser profilometer

Surface topographies of the replica surfaces were evaluated using a non-contact laser profilometer (LPM) (UBM Microfocus; UBM Messtechnik GmbH, Ettlingen, Germany) (Figs 4.2 and 4.3).

The profilometer has a 50-mm XY translation stage and this particular instrument was fitted with a UBM microfocus sensor (autofocusing system, 2 mm working distance, 1 mm range, 0.1 μm resolution in the Z axis). It uses infrared radiation (λ= 780 nm) from a semiconductor laser, whose power can be set to match the expected reflection for the object surface. The instrument employs the principle of dynamic focusing to determine the height of the surface from an arbitrary origin. While the specimen is scanned on the translation stage, a servo system maintains the focus condition by adjusting the objective lens height at each point measured. The instrument maintains this focus condition in which the infrared beam is always focused onto the measurement surface as a spot approximately 1 μm in diameter. This spot is then imaged onto four photodiodes within the sensor using a beam splitter lens and prism arrangement. The photodiode outputs are used to give a focus error signal which is used to move the position of the objective until the error signal is minimized. The displacement of the lens gives the change in height of the surface (resolution 0.1 μm) using a second measuring system attached to the objective. An advantage of the dynamic focusing sensor is that the instrument can simultaneously measure the surface reflectivity at each point because of the importance of measuring reflection from the surface rather than the depth of specimen. The measurement results are insensitive to surface reflectivity provided more than 2% of the incident light returns. Both the optical sensor and the translation stage are under computer control. The operational software also includes an analysis package which was used to calculate surface roughness parameters from the measured line scans.

Figure 4.2 UBM non-contact laser profilometer (LPM).

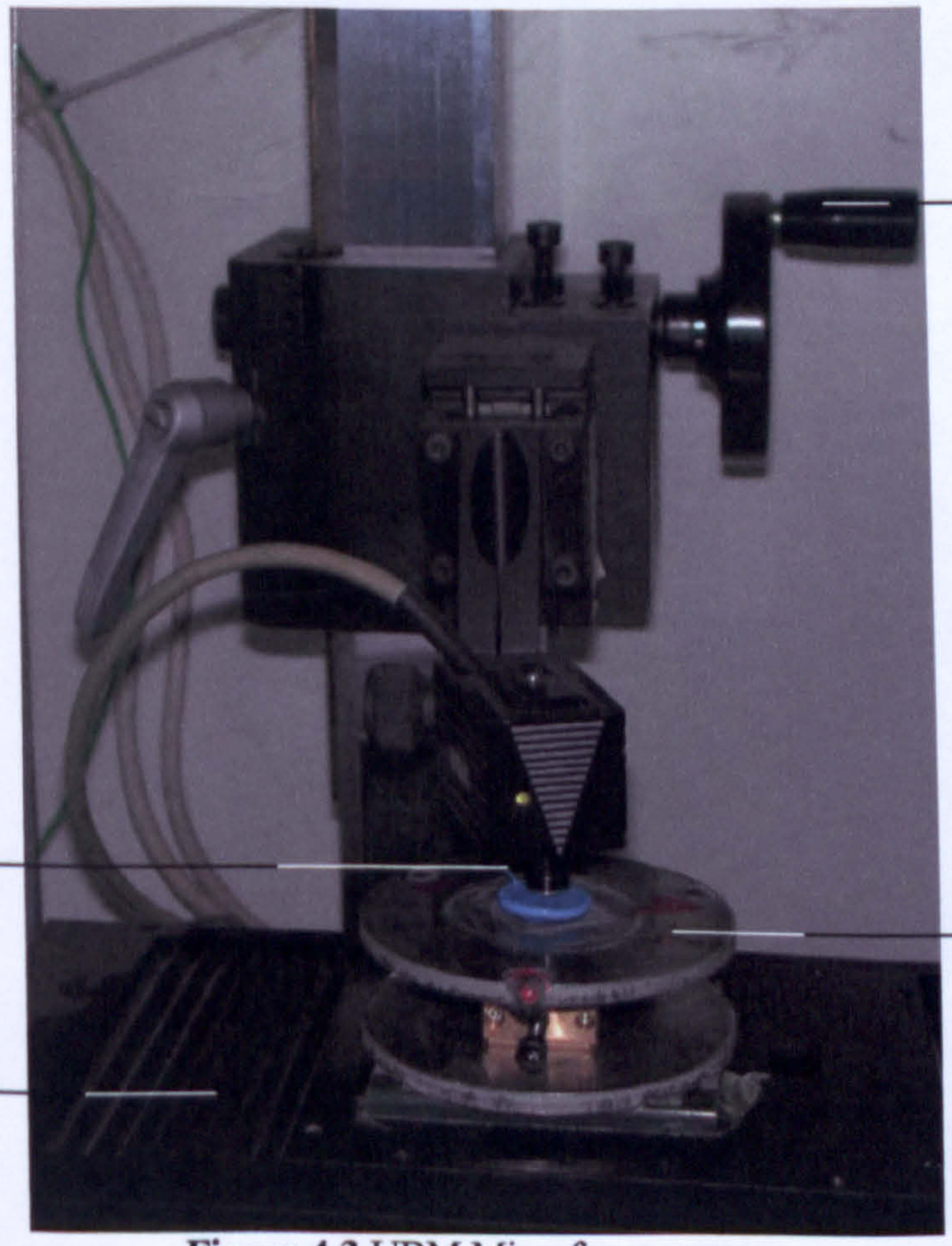


Figure 4.3 UBM Microfocus sensor.

4.3.2.3 Line Scan Parameters

Three test specimens of each material at different immersion times were randomly obtained and each measurement was taken at random spots on each replica surface. The measurement area was 2.0 mm x 2.0 mm, which gives an area of 4.0 mm^2. Three lines on the specimen were measured over distance of about 2 mm. All line scans on all specimens were performed with the following measurement parameters: scan area 2 mm x 2 mm; search speed 0.5 mm s^{-1}; point density 2,000 points mm^{-1} (X axis) and 1 point mm^{-1} (Y axis); reflection-low threshold 1.2%. Each line scan took 5 minutes to complete. All measurements were carried in ambient atmosphere and room temperature.

The profile was treated with a Gaussian filter and an attenuation factor of 50% at the cut-off wavelength of 0.36 mm to separate waviness from roughness using the software provided with the LPM (UBM; UBM Messtechnik GmbH). After that, integral roughness parameters were calculated within the UBM software. For characterization of the specimen's surface roughness, two parameters (R_a: arithmetic average roughness and R_q: root mean square roughness) and one extreme height parameter (R_{max}: maximum roughness depth) were chosen (see Figure 4.4). Where L is the evaluation length, and $Z(x)$ the profile height function, which is used to represent the point-by-point deviations between the measured profile and the reference mean line.

The average roughness (R_a), describes the overall surface roughness, and can be defined as the arithmetic average of the area between the roughness profile and its mean line or the integral of the absolute value of the roughness profile height over the evaluation length.

$$Ra = \frac{1}{L}\int_0^L |Z(\chi)|\, d\chi \qquad (4.7)$$

The root mean square roughness (R_q) represents the geometric average roughness component irregularities measured from the mean line within in the evaluation length and it is more sensitive to occasional peaks and valleys.

$$Rq = \sqrt{\frac{1}{L}\int_0^L Z(\chi)^2 \, d\chi} \qquad (4.8)$$

The maximum roughness (R_{max}) defined as the largest single roughness depth within the evaluation length.

The statistical differences between test groups were analysed by the non-parametric Mann-Whitney U test for comparing two independent samples and the Kruskal-Wallis One Way Analysis of Variance on Ranks for comparing three or more independent samples, and Turkey's test at a 0.05 significance level. Statistical analysis was carried out using SigmaStat® Statistical software for Windows version 3.0.

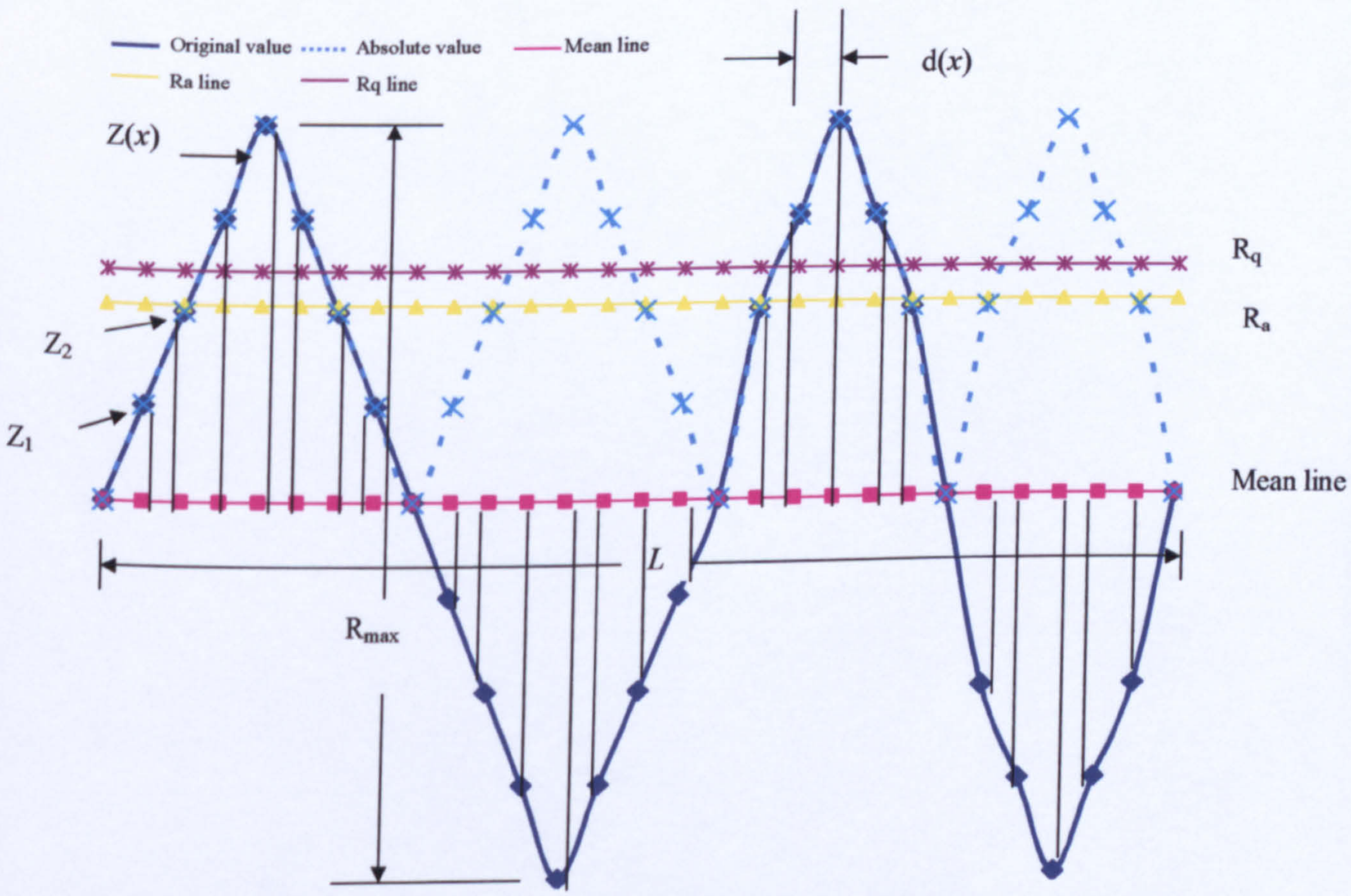


Figure 4.4 Illustration for the three surface roughness parameters; R_a, R_q and R_{max}. (R_a = Average deviation of roughness profile $Z(x)$ from the mean line = Total shaded area/L.)

4.3.3 Wettability (Contact Angle)

The wettability of a solid by a liquid is measured by determining the contact angle, θ, between a drop of the liquid and a plane surface of the solid (Wright 1980). As θ increases from 0 so the surface tension of the liquid rises, when θ is equal to 0, the liquid wets the solid completely. The tendency for the liquid to spread increases as the contact angle, θ, decreases. Contact angle measurement was used to examine the surface energy and tension related to wetting and adhesion of material surfaces. The degree of surface wetting corresponds to the surface energy of the material, and the drop contact angle varies inversely with its wetting capability. A simple standard approach was used in order to give the best opportunity of comparing contact angles for different materials. Using the sessile drop method (examining the contact angle of a static droplet), a droplet is placed on a flat, horizontal surface that can spread until it reaches equilibrium on the surface. This gives an advancing contact angle, even though the droplet is static at time of measurement.

At time of measurement, specimens were evaluated with no surface preparation and particular care was taken not to handle the surfaces of the specimens to be tested. Contact angles were measured by an Intel®Play™ Qx3 Computer Microscope (Figure 4.5) (Mattel Inc, Ca 90245, USA, Intel®Play™ Products, WI 53547, USA) with UTHSCSA ImageTool™ software version 3.1 (developed at the University of Texas Health Science Centre at San Antonio, Texas, USA) connected to a personal computer (Figure 4.6). Specimens were placed on to a movable stage (giving control of X and Y directions). A focus control was given by a camera mount that can be raised or lowered (giving control of Z direction). Using a 50-200µl Genex Beta pipette (VWR International™, BDH Laboratory Supplies, Leicestershire, UK), a 180µl sessile droplet of distilled water was carefully placed on the surface of the specimen. The image was refocused to give a sharp meniscus and then the image was subsequently captured for analysis (Figure 4.6). Since the initial contact between a drop and the surface to be measured generated some mechanical disturbance within the liquid, images were captured 10 seconds after the drop was deposited (Redey *et al.*, 2000), which was the estimated time required to attain equilibrium with the liquid that was used. Three contact angle measurements were made

on each specimen carried out at room temperature. Specimens were then immediately transferred to a bottle containing 50 ml of food simulating liquids and stored in an incubator (LABHEAT Model RLCH0400, Boro Labs Ltd, Berkshire, UK) at 37±1°C. Each specimen was removed at predetermined time intervals (Table 4.6), carefully blotted to remove excess surface liquid using filter paper prior to weighing and image capture. Initial intervals for measuring contact angles were short but subsequently increased. Statistical analysis of the contact angles among the materials and test periods, the materials and storage media were carried out using two-way ANOVA and Turkey's HSD multiple range tests at a 0.05 significance level. Statistical analysis was carried out using SigmaStat® Statistical software for Windows version 3.0.

Figure 4.5 The Intel®Play™ Qx3 computer microscope.

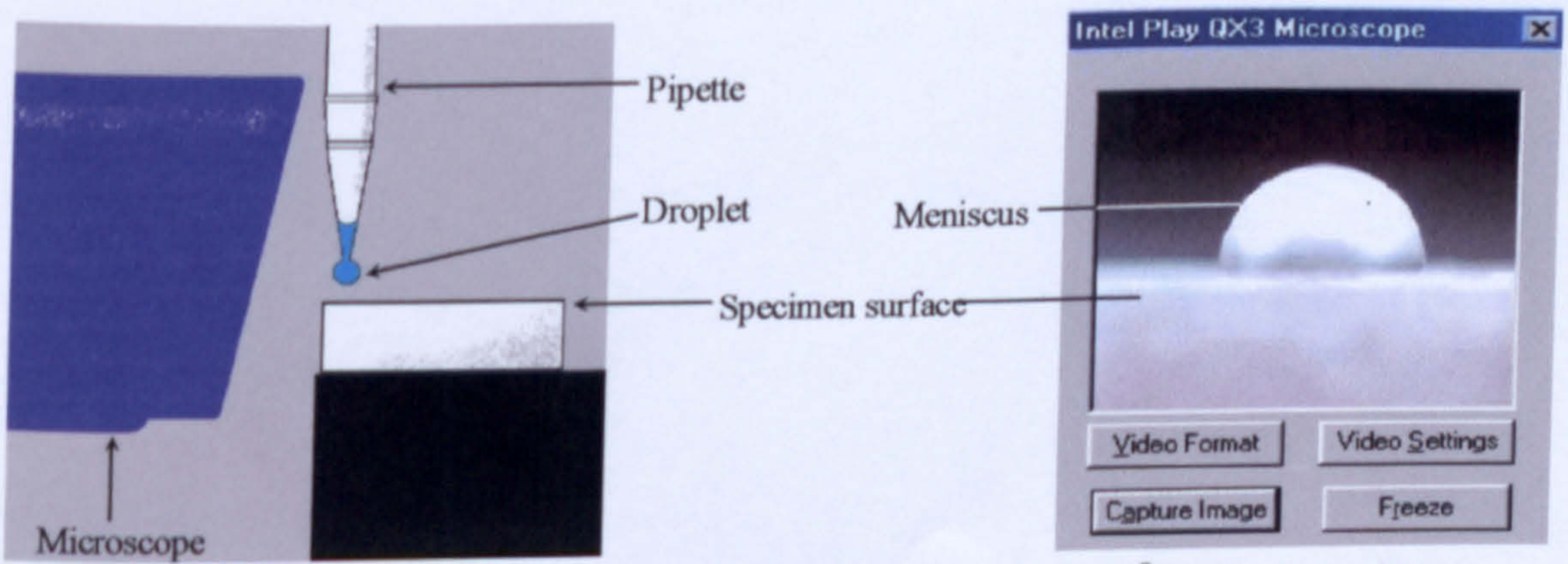


Figure 4.6 The sessile drop method and TWAIN interface for the Intel®Play™ Qx3 microscope opened by ImageTool™.

4.4 Mechanical characterisation

The resistance of a material to indentation or penetration can be measured as hardness. This method is an empirical test, hence no simple relationship exists between the hardness determined, and any fundamental property of the material tested. The method is based on the indentation of the specified indenter forced into the material under specific conditions. The relative hardness of elastic materials such as rubber or plasticised acrylics can be determined by a Shore A durometer (H17A Congenix Wallace Shore A Scale hardness tester; H W Wallace & Co. Ltd, Croydon UK) with Congenix Data Control software Version 1.1B connected to a 486 Type DX2 personal computer (Figure 4.7) at room temperature (23±1°C) on disc specimens (20 mm in diameter and 1 mm thick). This durometer consists of a blunt-pointed indenter, held in a vertical position, and the indenter located onto the surface of the specimens. This involved the application of a load to the indenter for a fixed period of time and measuring the elastic resistance to indentation. The reading was obtained 1 second after firm contact was achieved. If the indenter completely penetrates the sample, a reading of 0 is obtained. On the other hand, if no penetration occurs, a reading of 100 results. The more the indenter penetrates the specimen, the lower the hardness value obtained. The reading is dimensionless. Both the thickness of the specimen and the hardness of the supporting structure will affect the observed result. Therefore, in order to standardize conditions, the specimens were placed on a steel slab during testing.

Three readings were taken on each specimen at least 8 mm from the edge and 3 mm apart. Measurements were made at fixed time intervals after immersion (Table 4.6). In this case the specimen thickness was kept to one mm to match the specimen size for fluid sorption. This is less than that recommended for ASTM testing but provides a comparison of hardness with each material with respect to time. Indentation of elastomers, using such as the Wallace Shore A instrument, is essentially an elastic process, and hardness is related to Young's modulus (E). The formula for converting the Apparent Hardness (Ha) to the ASTM Shore Hardness (H) (see appendix A.2) is:

$$H = \frac{[H_a - 39.9]}{0.61} \qquad (4.9)$$

Young's modulus can be calculated below (Equation 4.10) adapted from Gent (1958);

$$E\ (MPa) = 0.0981(56+7.66s)/\ [0.137505(254-2.54s)] \qquad (4.10)$$

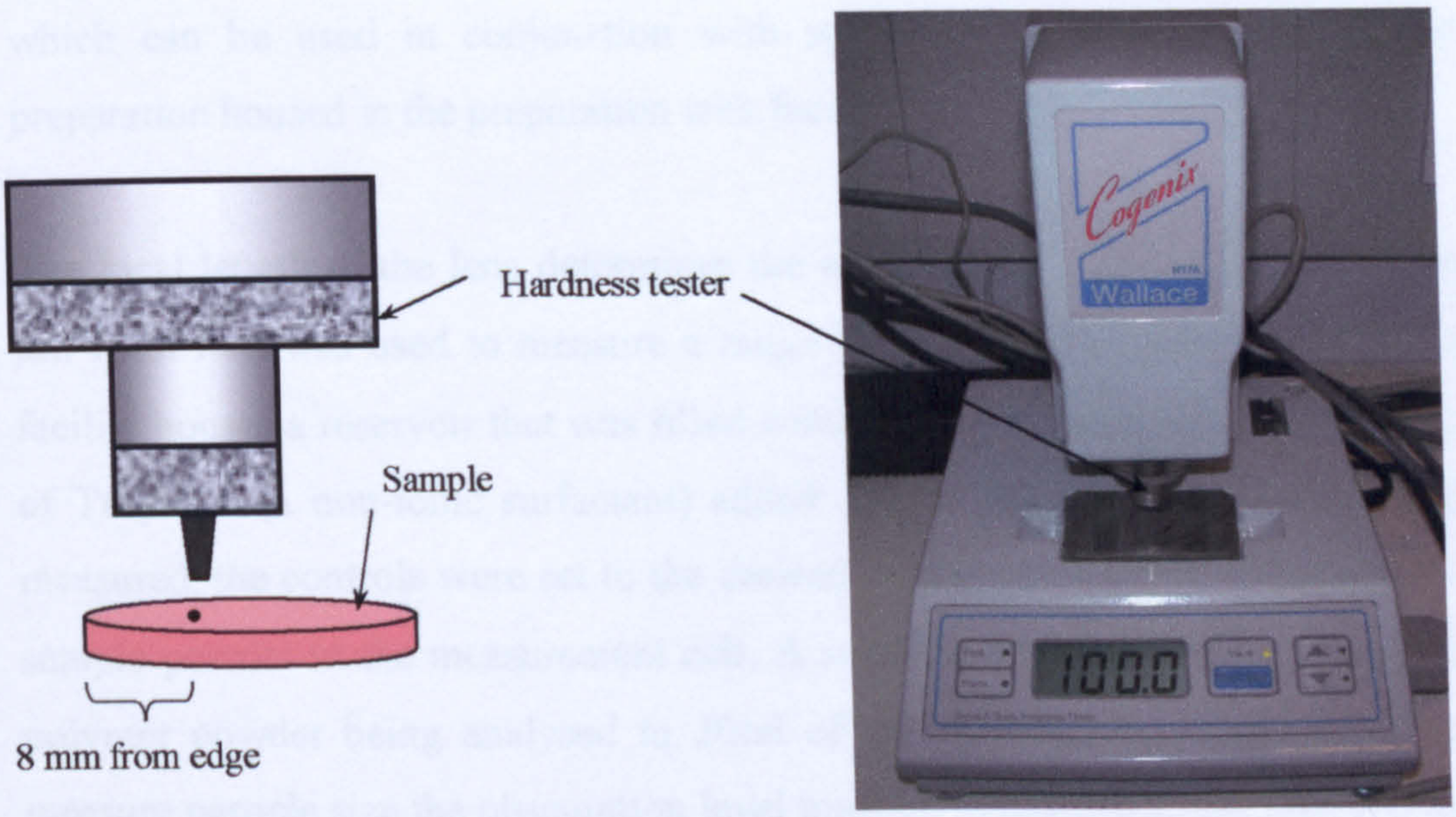


Figure 4.7 Wallace Hardness Durometer.

The statistical differences between test groups were analysed by the non-parametric Mann-Whitney U test for comparing two independent samples and the Kruskal-Wallis One Way Analysis of Variance on Ranks for comparing three or more independent samples, and Turkey test at a 0.05 significance level. Statistical analysis was carried out using SigmaStat® Statistical software for Windows version 3.0.

4.5 Particle Size Analysis

The science of particle technology combines the study of powders, aerosols, suspensions and emulsions. The distribution of particle diameters was assessed for Vertex™Soft and EverSoft®. A Malvern Mastersizer™ Type E particle size analyser (Malvern Instruments, Worcestershire, UK), connected to Malvern® PowerMate 286 Plus personal computer, was used to measure the distribution of mean particle sizes, which were contained in a water suspension (Figure. 4.8).

Wet dispersion was the method of analysis, and this involves ultrasound and surfactants to aid dispersion. There are a number of possible dispersing liquids (e.g. benzene,

ethanol, heptane, isopropyl alcohol, water, etc), where the choice depends on the sample being measured and the compatibility of different liquids that will reduce problems such as dissolution and aggregation. Ultrasound is a widely used technique for dis-aggregation, which can be used in conjunction with surfactants, and is applied during sample preparation housed in the preparation tank facility.

The focal length of the lens determines the range of the particles measured, thus a 300 μm focal lens was used to measure a range from 5.8 to 564 μm. The preparation tank facility houses a reservoir that was filled with 900 ml of water and another three droplets of Teepol L (a non-ionic surfactant) added. Before an initial background reading was measured, the controls were set to the desired levels in order to ensure circulation of the sample powder to the measurement cell. A solution was prepared by adding 2g of each polymer powder being analysed to 20ml of water, and six droplets of Teepol L. To measure particle size the obscuration level must be between 0.2 and 0.25 (no units). This was achieved by incremental addition of the test solution until the designated range was reached. The particle size of the sample was then analysed. This was then followed by a burst of ultrasound at level 10 for approximately 1 minute. The measurement cycle was repeated until the distribution became stable, which indicated complete dispersion. Cumulative frequency plots of particle size were obtained and subsequently used to calculate the mean and the distribution of particle diameters.

Figure 4.8 Malvern® Mastersizer Type E particle size analyser.

4.6 Characterisation of leachable substances

The analysis of leachable substances in the storage solution was done using a FTIR (Fourier Transform Infrared spectrometer) (Spectrum GX, PerkinElmer, Beaconsfield, Buckinghamshire, UK) with ATR (attenuated total reflection) (Zinc Selenide, Specac Inc, USA) element connected to a personal computer. A background spectrum was obtained and stored in the computer memory by directing the infrared beam through distilled water. Absorbance spectra were recorded at a resolution of 2 cm^{-1} average with 16 scans in the 500-4000 cm^{-1} range for both background and sample solutions and converted to absorption.

Reference spectra from food simulating liquids (DW, AS, 3AA, 10E, 50E, CO, and HB) (free of denture soft lining materials) were obtained in addition to spectra from solutions after storage. The spectrum of the leachable materials in each of the sample solutions was sought by subtraction of the appropriate reference solution absorbance from the sample absorbance spectrum.

Analysis of the spectra of the leachable substances was based on a three-part characterisation: vibrational frequencies, relative intensities, and shapes of the infrared absorption bands. Peak height comparison was done to determine whether an increase in leached components occurred with storage time. These results were compared qualitatively rather than quantitatively for this study. Descriptive changes rather than statistical analyses are provided.

4.7 Microbiological Characterisation

The purpose of this part of the investigation was to evaluate the treatment of commercial denture soft lining materials with oil in order to reduce the level of *Candida albicans* colonisation and to reduce friction between the lining and the mucosa. The hypothesis was that oil-treatment would reduce adherence of *Candida albicans* to the oil-treated denture soft lining materials.

4.7.1 Test specimens

Two methacrylate-based denture soft lining materials and two silicone-based denture soft lining materials were selected:

Vertex™Soft (Dentimex BV, Holland)

EverSoft® (Myerson, Austenal Ltd, UK)

Molloplast-B® (Karl Huber GmbH & Co. Germany)

Ufi Gel SC (Voco GmbH, Germany)

These were tested with and without the following sealers and oil treatment.

Ufi Gel SC sealer (Voco GmbH, Germany)

EverSoft® sealer (Myerson, Austenal Ltd, UK)

Coconut oil (Coconut oil from Cocos nucifera, C1758, Sigma Chemical Co. USA)

All denture soft lining materials were prepared in stainless steel moulds, lined with acetate sheets, by placing the mixed material in the centre of a mould comprising a 2 mm spacer which was sandwiched between two metal plates (Figure 4.9). On setting, the 2 mm thick sheet of denture soft lining material was then removed from the mould. Disc samples were cut from the sheet, 10 mm in diameter and 2 mm thick, using a cork borer. A total of 12 specimens were prepared for Molloplast-B®, Ufi Gel SC and Vertex™Soft, and 18 specimens were fabricated for EverSoft®. The specimens were then randomly divided into four (Molloplast-B®, Ufi Gel SC and Vertex™Soft) and six (EverSoft®) groups of three specimens.

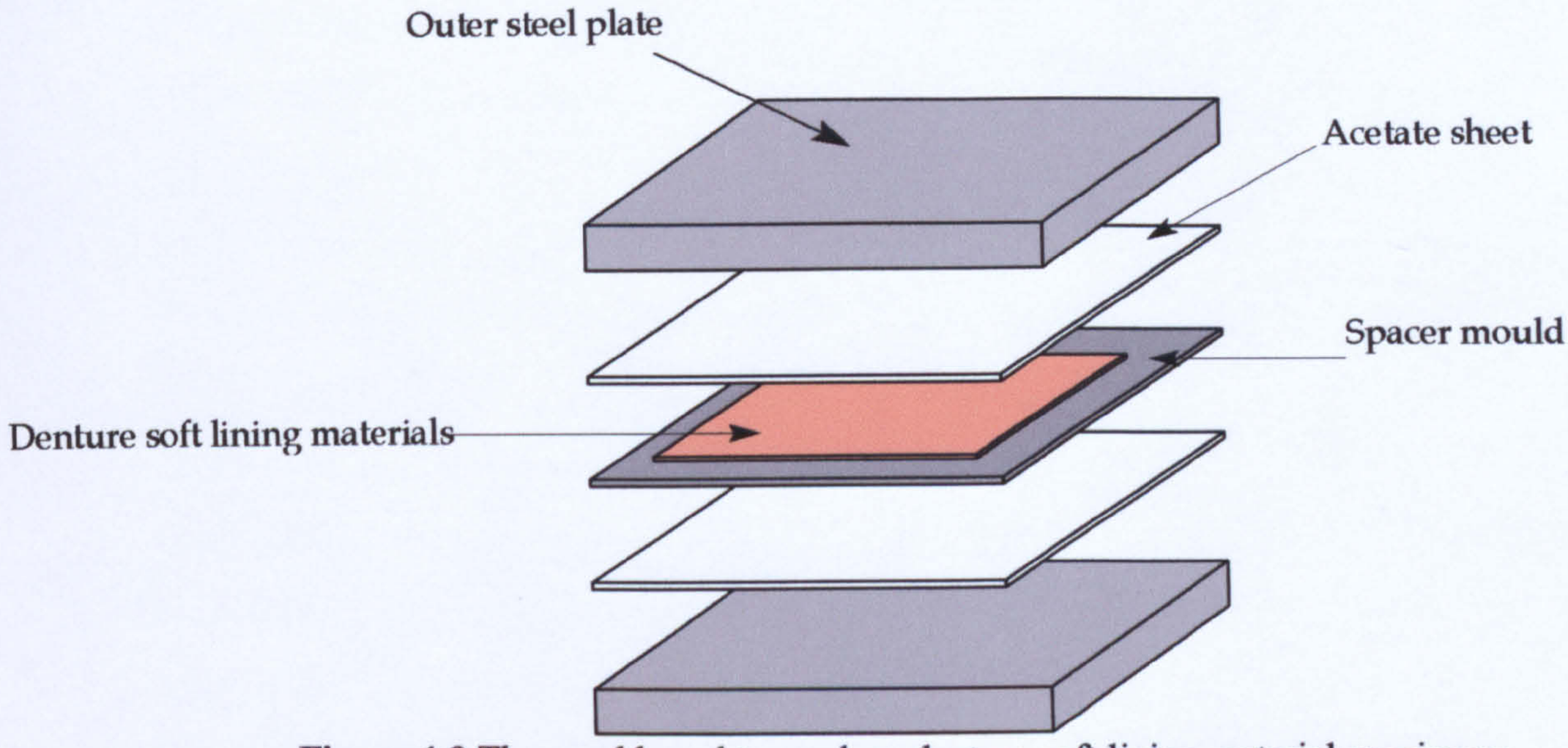


Figure 4.9 The mould used to produce denture soft lining material specimens.

The surfaces used to assess the effect of oil-treatment on adhesion were:

Molloplast-B®
(a) no glazing (**MBNC**)
(b) glazing with Ufi Gel SC sealer (**MBSC**)
(c) no glazing + oil-treatment (**MBNO**)
(d) glazing with Ufi Gel SC sealer + oil-treatment (**MBSO**)

Ufi Gel SC
(a) no glazing (**UGNC**)
(b) glazing with Ufi Gel SC sealer (**UGSC**)
(c) no glazing + oil-treatment (**UGNO**)
(d) glazing with Ufi Gel SC sealer + oil-treatment (**UGSO**)

Vertex™Soft
(a) no glazing (**VTNC**)
(b) glazing with Ufi Gel SC sealer (**VTSC**)
(c) no glazing + oil-treatment (**VTNO**)
(d) glazing with Ufi Gel SC sealer + oil-treatment (**VTSO**)

EverSoft®
(a) no glazing (**ESNC**)
(b) glazing with EverSoft® sealer (**ESTSC**)
(c) glazing with Ufi Gel SC sealer (**ESSC**)
(d) no glazing + oil-treatment (**ESNO**)
(e) glazing with EverSoft® sealer + oil-treatment (**ESTSO**)
(f) glazing with Ufi Gel SC sealer + oil-treatment (**ESSO**)

EverSoft® sealer, a methyl ethyl ketone, was applied unidirectional over the whole surface of six randomly chosen EverSoft® specimens with a soft brush in a thin, even layer for 2 minutes and allowed to air dry at room temperature. Ufi Gel SC sealer was applied unidirectional to six specimens of Molloplast-B®, Ufi Gel SC , Vertex™Soft and EverSoft® with a soft brush in a thin, even layer for 2 minutes and allowed to air dry at room temperature. The disc specimens were sterilized with microwave irradiation for 6 minutes at 650 W output in a conventional microwave oven. Coconut oil was sterilized independently by autoclave. In an environmental chamber, the sterilized coconut oil was poured into a sterilized syringe fitted with a filter (0.2 μm syringe; Non-Pyrogenic; Schleicher & Schuell), then the sterilized coconut oil was injected over the specimen's surface evenly and left standard for the discs to be immersed in the sterilized coconut oil for 5 minutes prior to removing excess oil by blotting with sterile blotting paper.

4.7.2 Microbiological procedures

4.7.2.1 *Candida albicans* growth

Candida albicans strain NCYC 1467 (from denture-related stomatitis) was obtained as a stock culture from Oral Microbiology, Bart's and The London, University of London. Stock cultures were maintained on Sabourauds dextrose agar slopes (Oxoid, Ltd., Basingstoke, Hants) at room temperature. A loopful of stock culture was streaked onto Sabourauds dextrose agar (SAB) plates and incubated aerobically at 37±1°C for 24 hour. One loopful of this fresh yeast growth was then inoculated into 10 ml Sabourauds liquid medium and incubated at 37±1°C on an shaker at 120 rpm, overnight. SAB agar plates were inoculated with 30 µl of the *Candida albicans* overnight culture from Sabouraud broth adjusted to an $O.D_{600nm}$ =1.2 with fresh Sabourauds liquid medium (≡ $1x10^7$ cells mL^{-1}) and spread evenly over the surface with a sterile glass spreader. The prepared disc specimens were then placed onto the agar surface, and the plates with test discs were incubated aerobically for 24 hours at 37±1°C.

4.7.2.2 Adhesion assay

After incubation, each disc was removed and washed three times with 10 ml PBS (phosphate buffered saline) to remove non-adherent yeasts. After washing, 5 ml fresh

sterile Sabourauds liquid medium was added to each disc together with 20 sterile glass beads (3.5 to 4.5 mm, Merck). These were vigorously shaken by vortexing in the centrifuge for 1 minute to dislodge attached *Candida albicans* cells. These liquids with re-suspended cells were then plated onto SAB plates using a spiral plater (Spiral Plater: Model C, Don Whiteley) and incubated aerobically for 24 hours at 37±1°C in order to obtain viable yeast cell counts.

4.7.2.3 Statistical analysis

The statistical differences between test groups were analysed by a nonparametric Mann-Whitney U test for comparing two independent samples and the Kruskal-Wallis H test for comparing three or more independent samples, using SigmaStat® Statistical software for Windows version 3.0. A P value of < 0.05 was considered statistically significant.

CHAPTER FIVE

RESULTS

5.1 Fluid Absorption Characterisation

5.1.1 Fluid uptake of specimens stored in an unchanged storage medium

Tables 5.1-7 show the percentage weight change, weight loss and real fluid uptake of specimens on immersion in seven food simulating liquids (distilled water, artificial saliva, 3% acetic acid, 10% ethanol, 50% ethanol, coconut oil and HB307) after one year storage at 37±1°C. In this section the immersing fluids were unchanged through the study. The statistical analysis showed significant differences in percentage weight change, percentage weight loss, and real percentage uptake with time for each material and storage condition ($p<0.05$).

5.1.1.1 Fluid uptake of specimens stored in distilled water

Table 5.1 Summary of the fluid uptake of materials after one year storage in distilled water (no change of solution), mean (sd), (n=6)

Materials	% Weight change /DW	% Weight loss /DW	% Real uptake /DW	Diffusion coefficient D_{abs} (10^{-13} m^2sec^{-1})
Vertex™Soft	3.08 (0.39)	1.26 (0.12)	4.34 (0.39)	0.17
EverSoft®	4.83 (0.34)	13.45 (0.44)	18.28 (0.68)	*
Molloplast-B®	2.00 (0.11)	-1.36 (0.12)	0.64 (0.05)	4.68
Ufi Gel SC	1.92 (0.24)	-1.43 (0.24)	0.50 (0.04)	5.33
BE	9.71 (1.86)	-0.29 (0.13)	9.42 (1.86)	*

* Diffusion coefficient for EverSoft® and BE could not be determined since no equilibrium had been reached.

Table 5.1 exhibits that the denture soft lining materials increased in weight by up to 4.8% (ES) while the BE increased even more (9.7%). The increase in weight of each material differed significantly from the others tested ($p<0.05$), the ranking being BE > ES > VT > MB > UG. Figure 5.1 shows that MB and UG reached equilibrium with water within seven days; the weight the specimens remained nearly constant for the remainder of the test period. The weight of VT and ES continued to increase up to seven days and then remained nearly constant up to one month after which the weight increase continued. BE also showed a continuous increase in weight up to one year. Since the specimens of ES and BE stored in distilled water had not reached equilibrium, the sorption parameters of these specimens could not be calculated. Although it was not clear whether VT had reached equilibrium, the changes were very small and so a diffusion coefficient was calculated. Longer immersion would be needed to clarify this result.

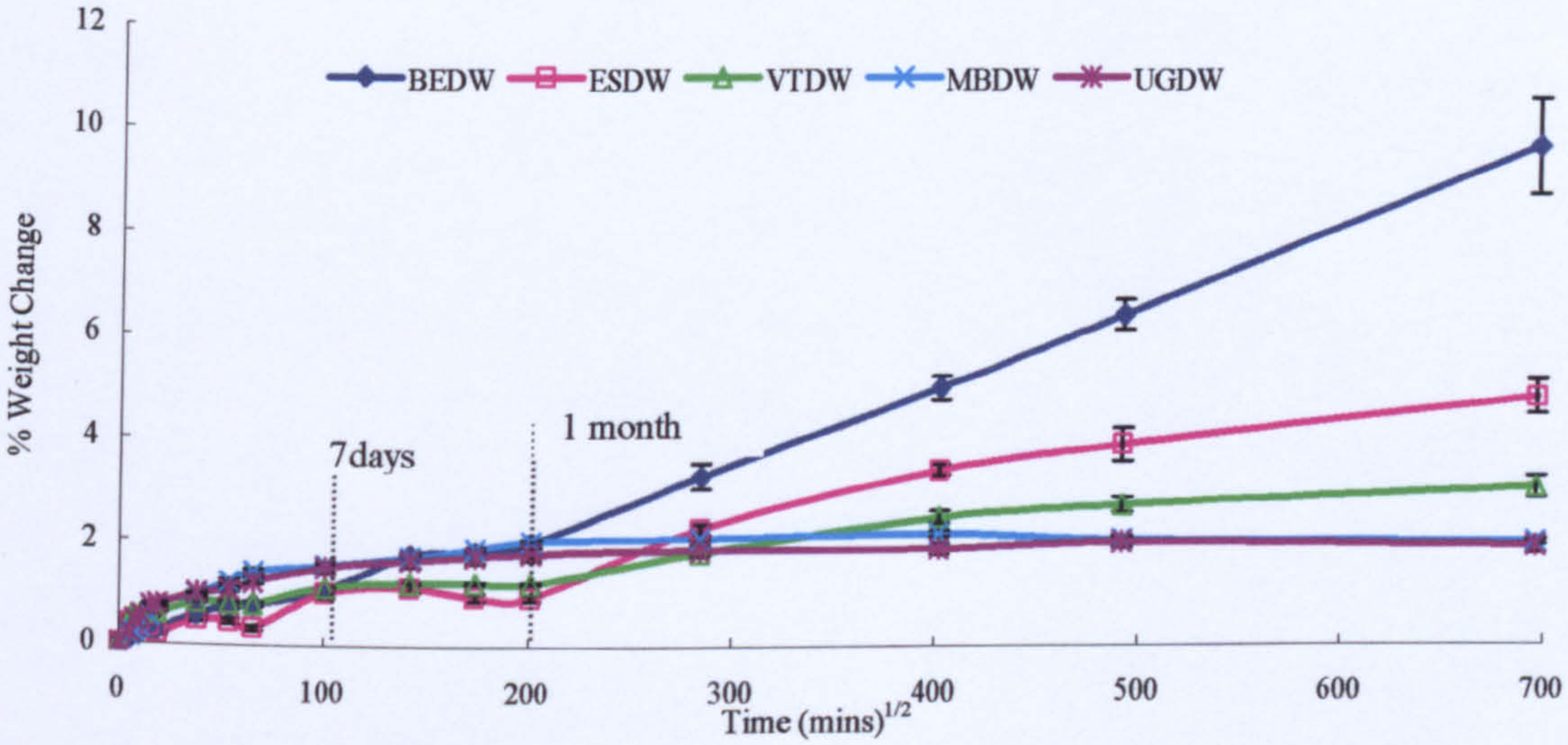


Figure 5.1 Mean percentage weight change of materials stored in distilled water.

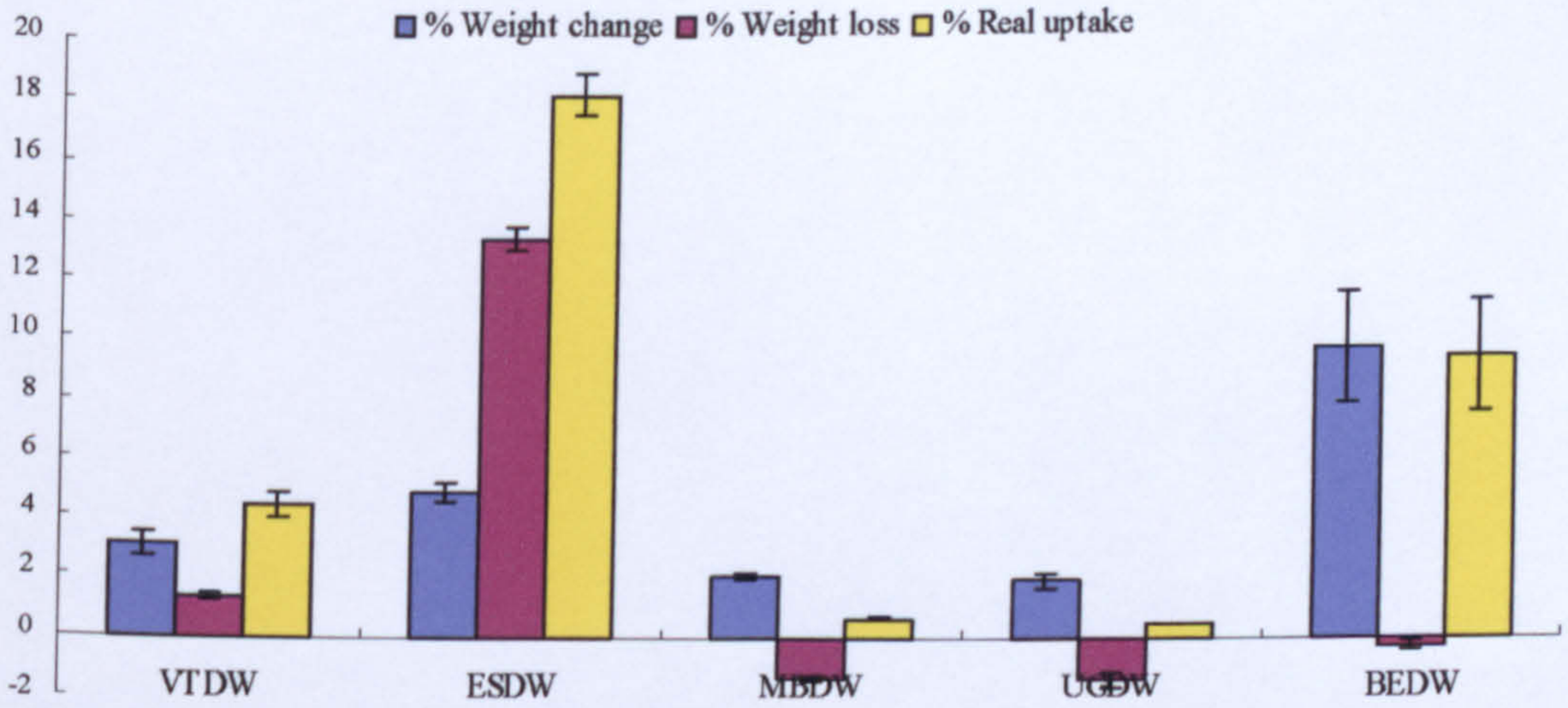


Figure 5.2 Bar chart of % weight change, weight loss, and real uptake of materials in distilled water at one year.

Figure 5.2 shows the percentage weight change, weight loss and real uptake in distilled water at one year. The highest percentage weight change was observed with BE, followed by ES and VT, then by MB and UG. No significant difference was observed in percentage weight change between ES and VT, and between MB and UG ($P > 0.05$). For MB and UG, the final weight after desorption was greater than its initial weight. A higher weight loss was observed in ES compared to VT. Additionally, the real percentage uptake of ES and BE was significantly higher than VT, MB and UG ($P < 0.05$).

5.1.1.2 Fluid uptake of specimens stored in artificial saliva

Table 5.2 Summary of the fluid uptake of specimens after one year storage in artificial saliva (no change of solution), mean (sd), (n=6)

Materials	% Weight change /AS	% Weight loss /AS	% Real uptake /AS	Diffusion coefficient D_{abs} (10^{-13} m^2sec^{-1})
Vertex™Soft	-2.94 (1.26)	7.93 (1.11)	4.99 (0.40)	*
EverSoft®	-5.90 (0.63)	16.38 (0.45)	10.48 (0.47)	*
Molloplast-B®	2.31 (0.21)	-1.17 (0.15)	1.14 (0.14)	8.58
Ufi Gel SC	1.48 (0.15)	-0.80 (0.13)	0.68 (0.03)	31.32
BE	7.13 (1.32)	0.39 (0.40)	7.52 (1.02)	*

* Diffusion coefficient for Vertex™Soft, EverSoft® and BE could not be determined since no equilibrium had been reached.

Figure 5.3 shows that MB and UG reached equilibrium within seven days; the weight of the specimens after this time remained nearly constant up to one year. The weight of VT and ES increased for seven days and then remained constant for up to four months. After this period a weight loss was observed. The final weight of VT and ES was less than the starting weight after one year. BE showed a continuous increase in weight up to one year. No equilibrium was reached at one year for VT, ES and BE. Hence the sorption parameters of these specimens could not be calculated.

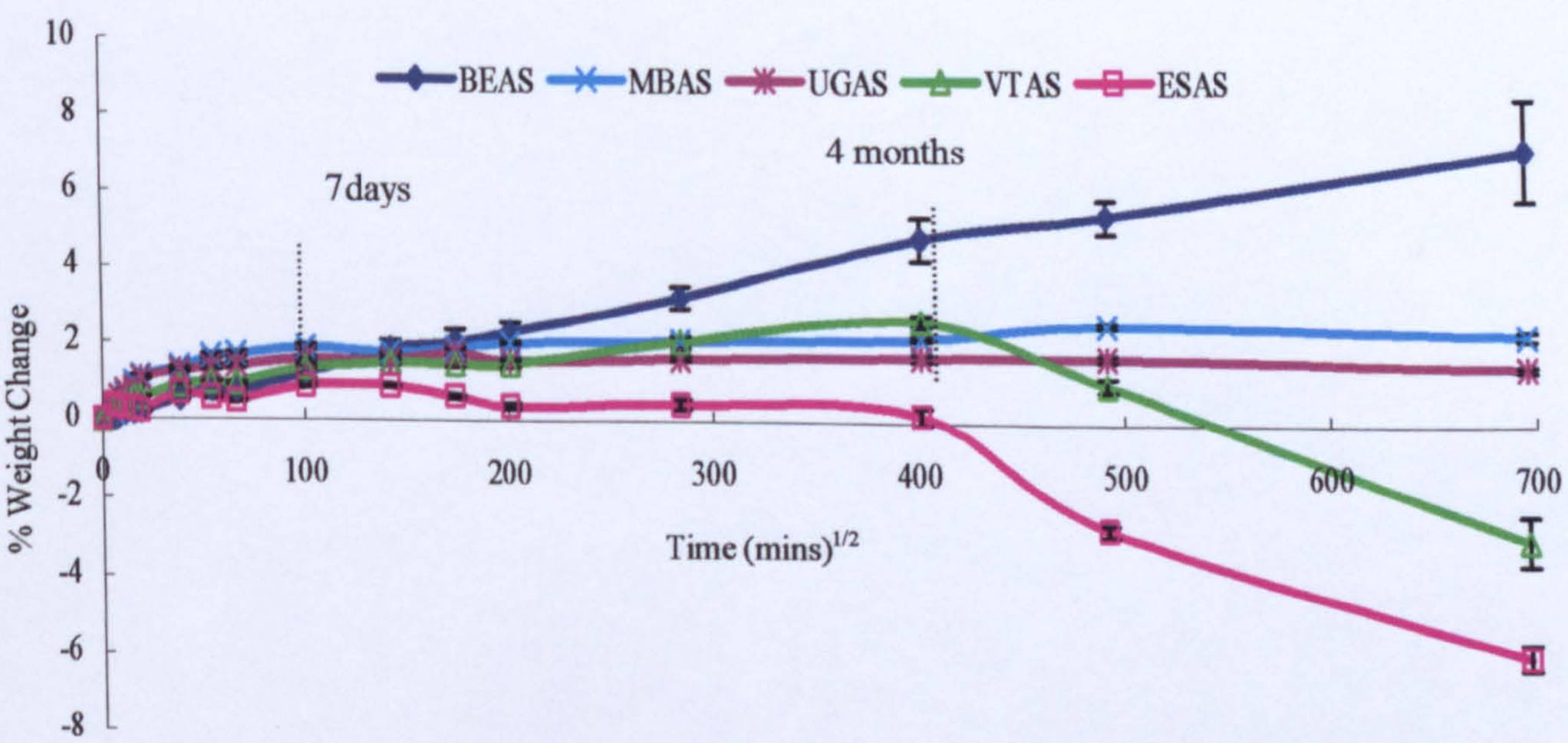


Figure 5.3 Mean percentage weight change of materials stored in artificial saliva.

Table 5.2 and Figure 5.4 show the overall percentage weight change, weight loss and real uptake in artificial saliva at one year. The highest weight increase was observed with BE. An overall weight loss was observed for ES and VT. No significant difference was observed in weight change between ES and VT, and between MB and UG ($P > 0.05$). For

MB and UG, the final weight after desorption was greater than its initial weight. A greater weight loss was observed in ES and VT compared to BE. Additionally, the real percentage uptake of ES, BE and VT was significantly higher than MB and UG ($P < 0.05$).

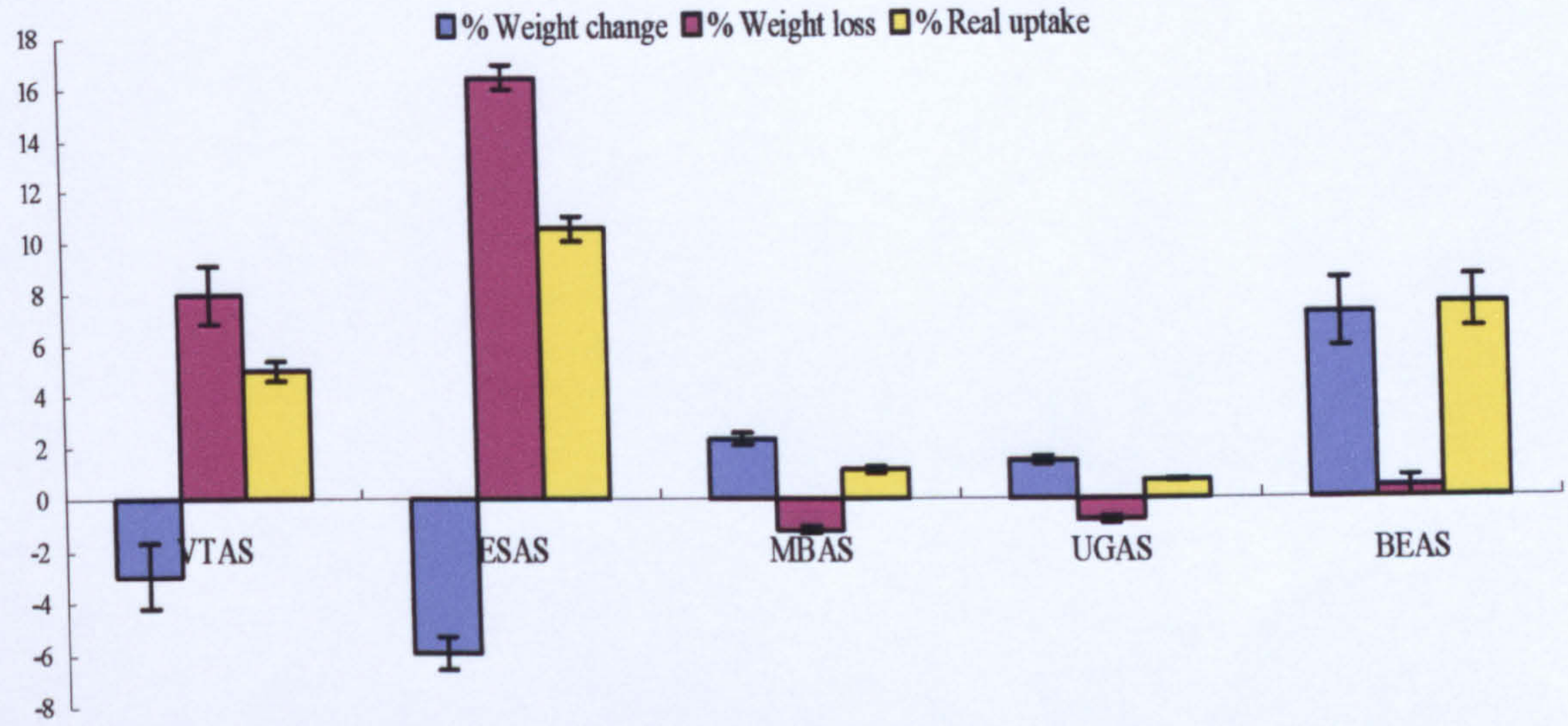


Figure 5.4 Bar chart of % weight change, weight loss, and real uptake of materials in artificial saliva at one year.

5.1.1.3 Fluid uptake of specimens stored in 3% acetic acid

Table 5.3 Summary of the fluid uptake of materials after one year storage in 3% acetic acid (no change of solution), mean (sd), (n=6)

Materials	% Weight change /3AA	% Weight loss /3AA	% Real uptake /3AA	Diffusion coefficient D_{abs} (10^{-13} m^2sec^{-1})
Vertex™Soft	13.10 (1.21)	1.51 (0.10)	14.61 (1.19)	*
EverSoft®	19.23 (1.39)	11.26 (0.75)	30.48 (1.84)	*
Molloplast-B®	3.13 (0.16)	-2.00 (0.16)	1.13 (0.07)	4.72
Ufi Gel SC	1.80 (0.18)	-0.92 (0.18)	0.88 (0.08)	4.39
BE	26.00 (1.21)	-0.25 (0.46)	25.75 (1.10)	*

* Diffusion coefficient for Vertex™Soft, EverSoft® and BE could not be determined since no equilibrium had been reached.

Figure 5.5 exhibits MB and UG absorbed less fluid than VT, ES and BE. MB and UG were again at equilibrium within seven days; subsequent to this period the weight of the specimens remained constant over this year test. Since the specimens of VT, ES and BE stored in 3 per cent acetic acid failed to reach equilibrium by one year, the sorption parameters of these specimens could not be calculated.

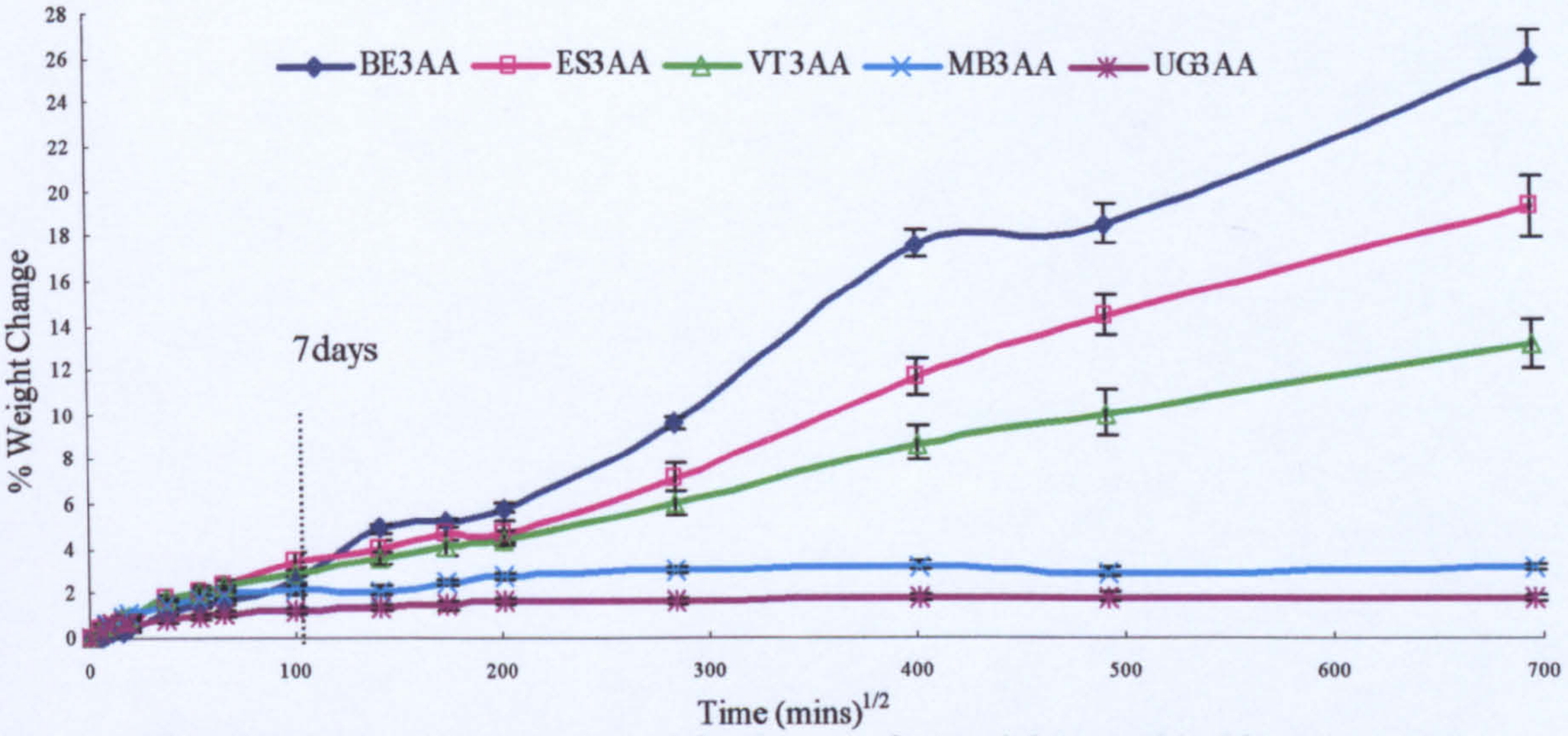


Figure 5.5 Mean percentage weight change of materials stored in 3% acetic acid.

Table 5.3 and Figure 5.6 show the overall percentage weight change, weight loss and real uptake following storage in 3% acetic acid at one year. Again the greatest weight change was observed with BE, followed by ES and VT, then by MB and UG. No significant difference was observed in weight change between ES and VT, and between MB and UG ($P > 0.05$). For MB, UG and BE, the final weight after desorption was greater than the initial weight. Of the two materials where weight loss occurred, ES showed a significantly greater loss than VT. The real percentage uptake of ES, BE and VT was significantly greater than MB and UG ($P < 0.05$).

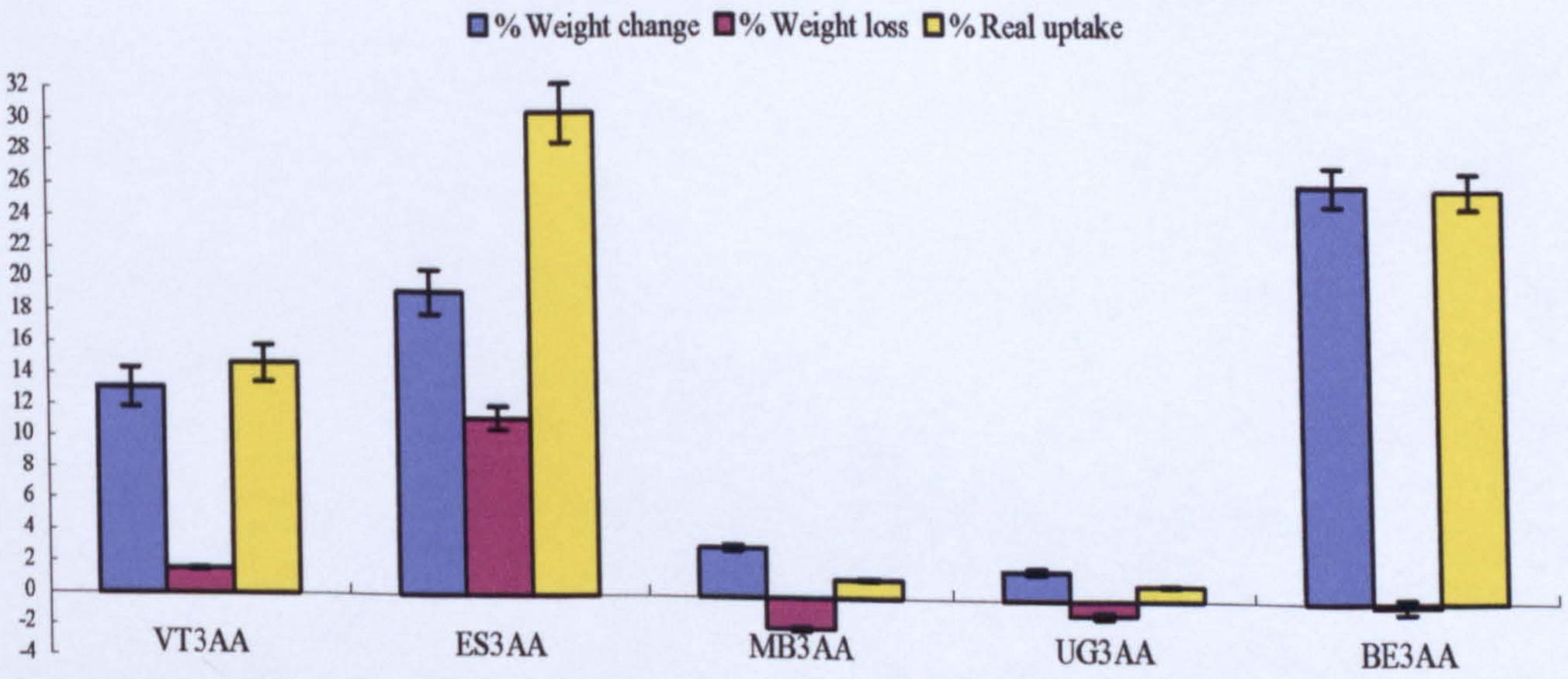


Figure 5.6 Bar chart of % weight change, weight loss, and real uptake of materials in 3% acetic acid at one year.

5.1.1.4 Fluid uptake of specimens stored in 10% ethanol

Table 5.4 Summary of the fluid uptake of materials after one year storage in 10% ethanol (no change of solution), mean (sd), (n=6)

Materials	% Weight change /10E	% Weight loss /10E	% Real uptake /10E	Diffusion coefficient D_{abs} (10^{-13} m^2sec^{-1})
Vertex™Soft	3.22(0.22)	0.94(0.24)	4.16(0.13)	2.68
EverSoft®	6.95(0.52)	13.48(0.36)	20.43(0.69)	*
Molloplast-B®	2.62(0.03)	-1.73(0.06)	0.89(0.04)	12.45
Ufi Gel SC	1.37(0.23)	-0.86(0.26)	0.51(0.03)	9.97
BE	12.48(1.14)	-0.30(0.17)	12.19(1.07)	*

* Diffusion coefficient for EverSoft® and BE could not be determined since no equilibrium had been reached.

Figure 5.7 shows that MB and UG had reached equilibrium at seven days. However, here VT also reached equilibrium within this period of time. The weight of all these specimens remained nearly constant for the remainder of the test period. The weight of ES and BE increased up to seven days and then remained constant for up to one month before continuing to increase in weight without reaching equilibrium even after one year. Hence, the sorption parameters of these specimens could not be calculated.

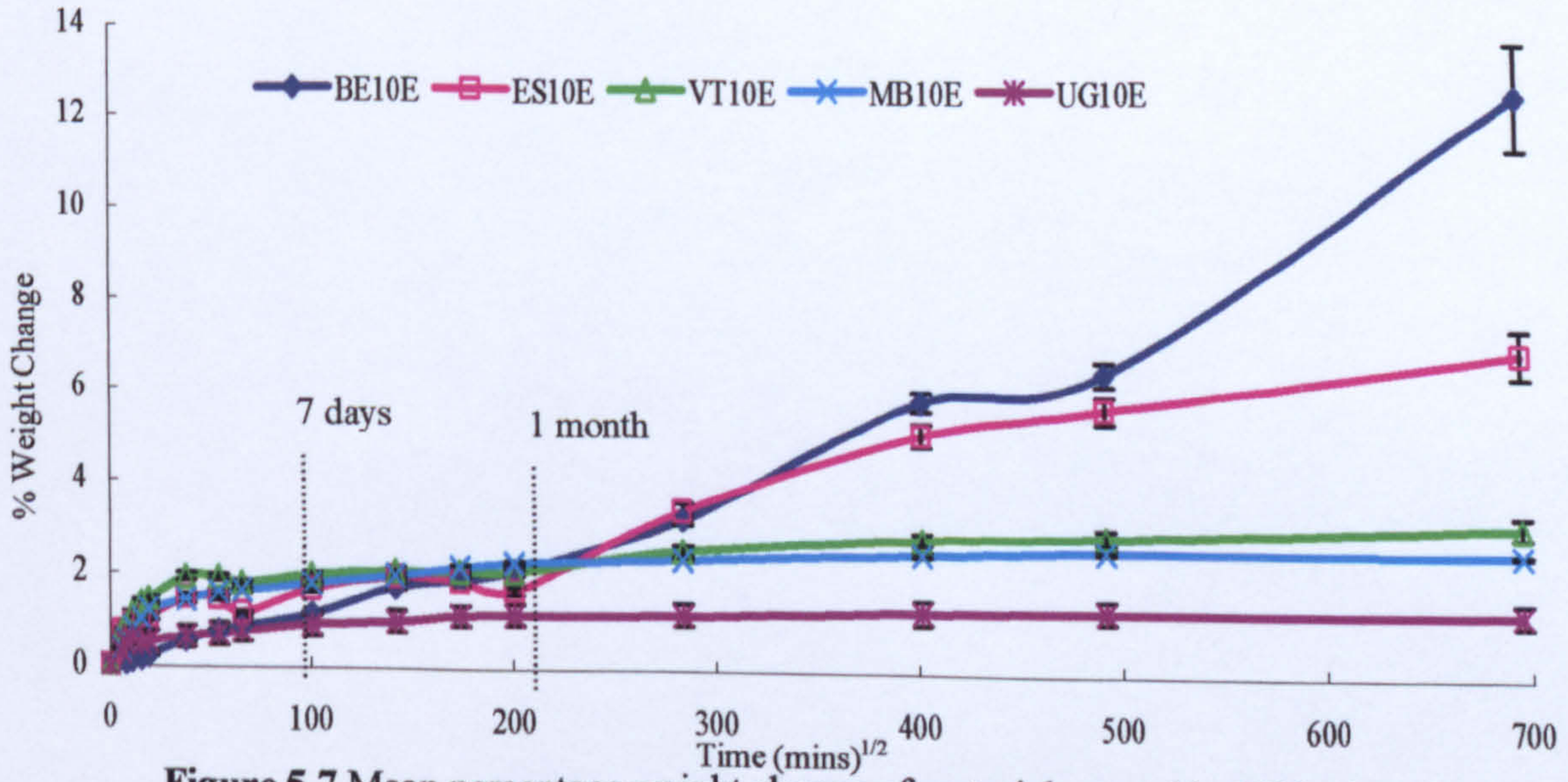


Figure 5.7 Mean percentage weight change of materials stored in 10% ethanol.

Table 5.4 and Figure 5.8 show the overall percentage weight change, weight loss and real uptake in 10% ethanol at one year. The greatest weight change was observed with BE. No significant difference was observed in weight change between ES and VT, and between MB and UG ($P > 0.05$). For MB, UG and BE, the final weight after desorption was greater than the initial weight. A greater weight loss was observed in ES. Additionally,

the real percentage uptake of ES and BE was significantly greater than VT, MB and UG, and VT was significantly greater than MB and UG ($P < 0.05$).

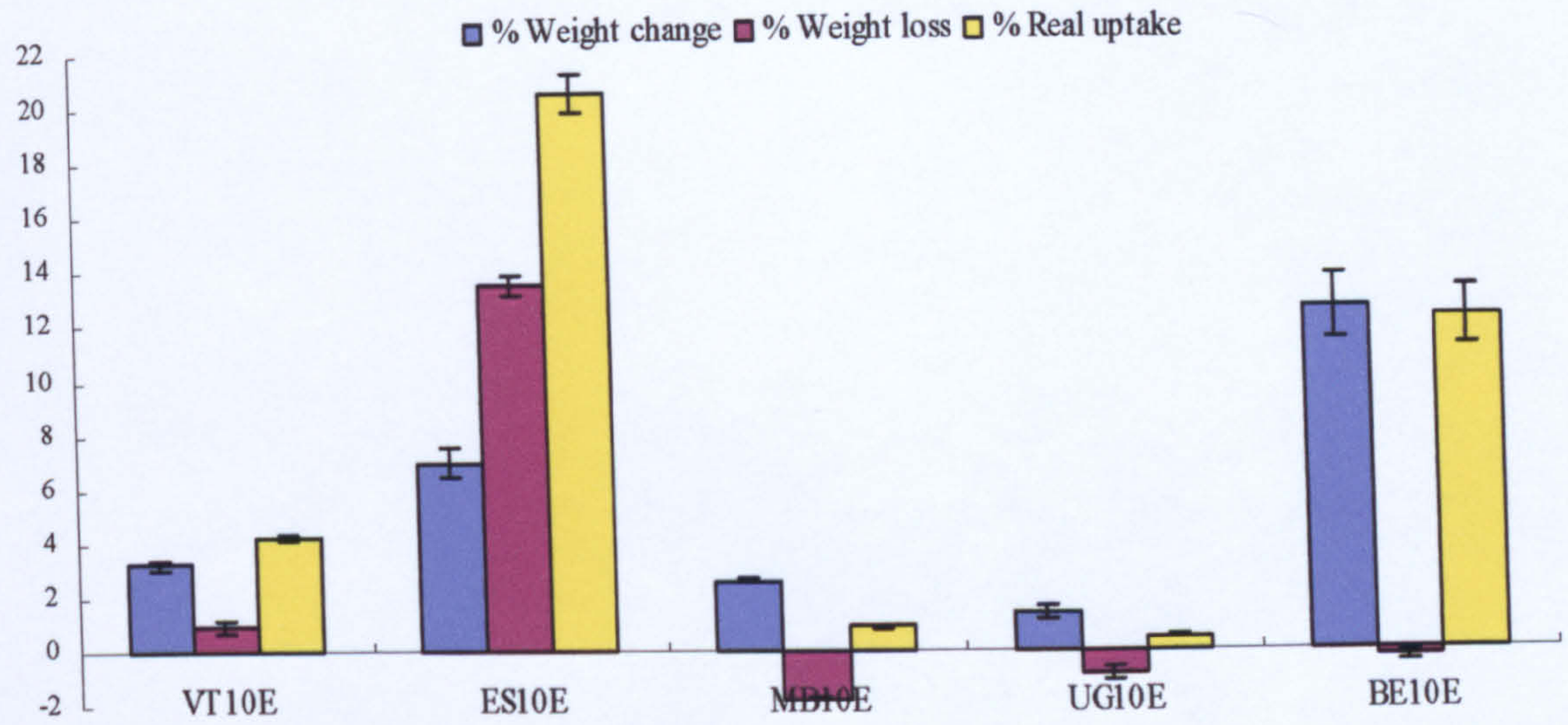


Figure 5.8 Bar chart of % weight change, weight loss, and real uptake of materials in 10% ethanol at one year.

5.1.1.5 Fluid uptake of specimens stored in 50% ethanol

Table 5.5 Summary of the fluid uptake of materials after one year storage in 50% ethanol (no change of solution), mean (sd), (n=6)

Materials	% Weight change /50E	% Weight loss /50E	% Real uptake /50E	Diffusion coefficient D_{abs} (10^{-13} m^2sec^{-1})
Vertex™Soft	4.58 (1.90)	6.33 (3.23)	10.90 (2.11)	*
EverSoft®	6.79 (2.64)	12.41 (0.81)	19.20 (2.37)	*
Molloplast-B®	2.68 (0.14)	-1.47 (0.15)	1.21 (0.05)	33.54
Ufi Gel SC	1.94 (0.08)	-1.32 (0.09)	0.62 (0.08)	50.84
BE	16.30 (1.11)	-0.67 (0.09)	15.63 (1.11)	*

* Diffusion coefficient for Vertex™Soft, EverSoft® and BE could not be determined since no equilibrium had been reached.

Figure 5.9 shows that MB and UG had equilibrated within three days. Thereafter the weight of the specimens remained stable for one year. The weight of VT and ES quickly increased in weight up to six hours, then showed a decrease in weight for one month, and then began to increase again. BE showed a continuous increase in weight up to one year. The two methacrylate-based denture soft lining materials and BE continue changing in weight and failed to reach equilibrium at one year. Since the specimens of VT, ES and BE stored in 50% ethanol had not reached equilibrium, the sorption parameters of these specimens could not be calculated.

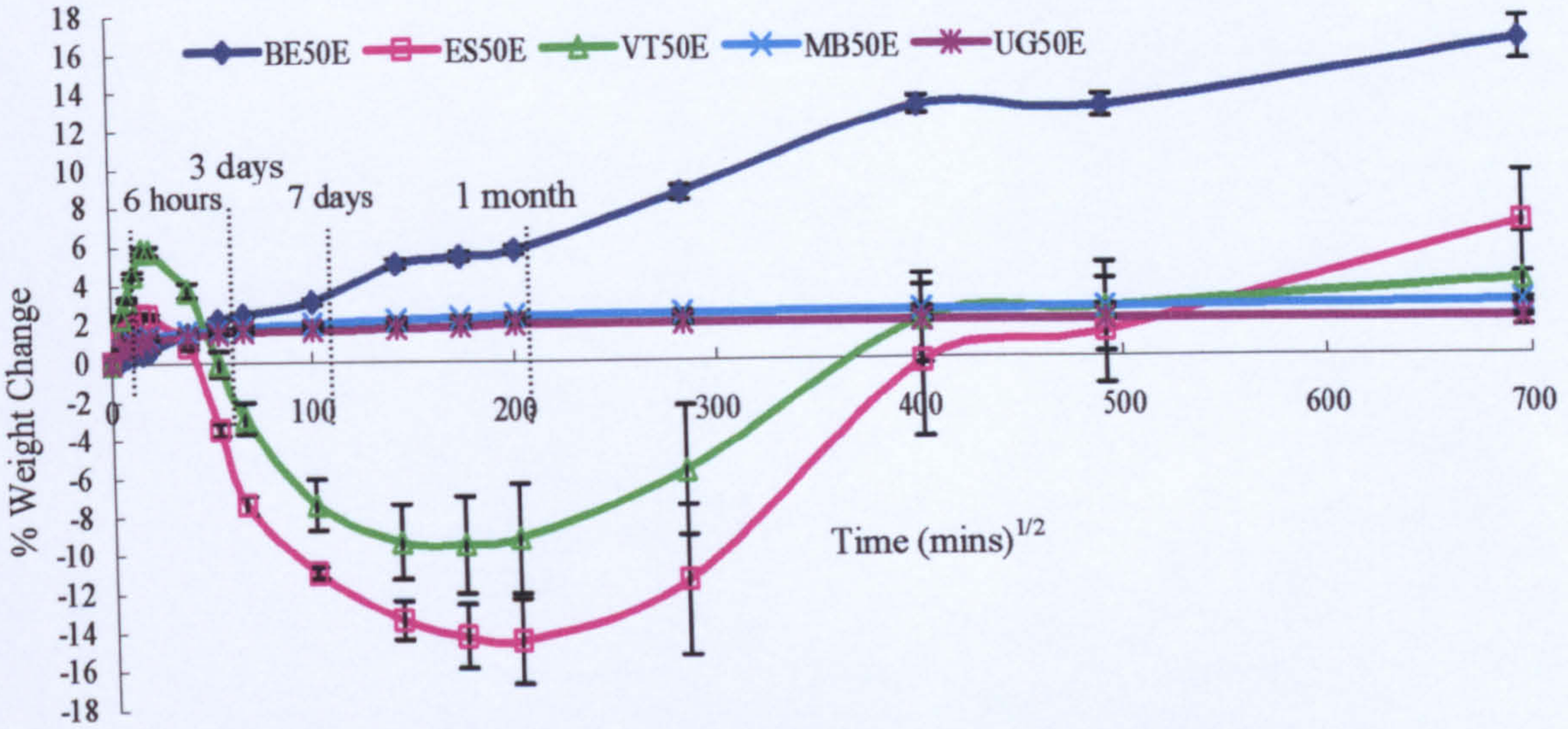


Figure 5.9 Mean percentage weight change of materials stored in 50% ethanol.

Table 5.5 and Figure 5.10 show the overall percentage weight change, weight loss and real uptake in 50% ethanol at one year. The greatest weight change was observed with BE. No significant difference was observed in percentage weight change between ES and VT, and between MB and UG ($P > 0.05$). For MB, UG and BE, the final weight after desorption was greater than the initial weight. A greater weight loss was observed in ES and VT. Additionally, the real percentage uptake of ES, BE and VT was significantly greater than MB and UG ($P < 0.05$).

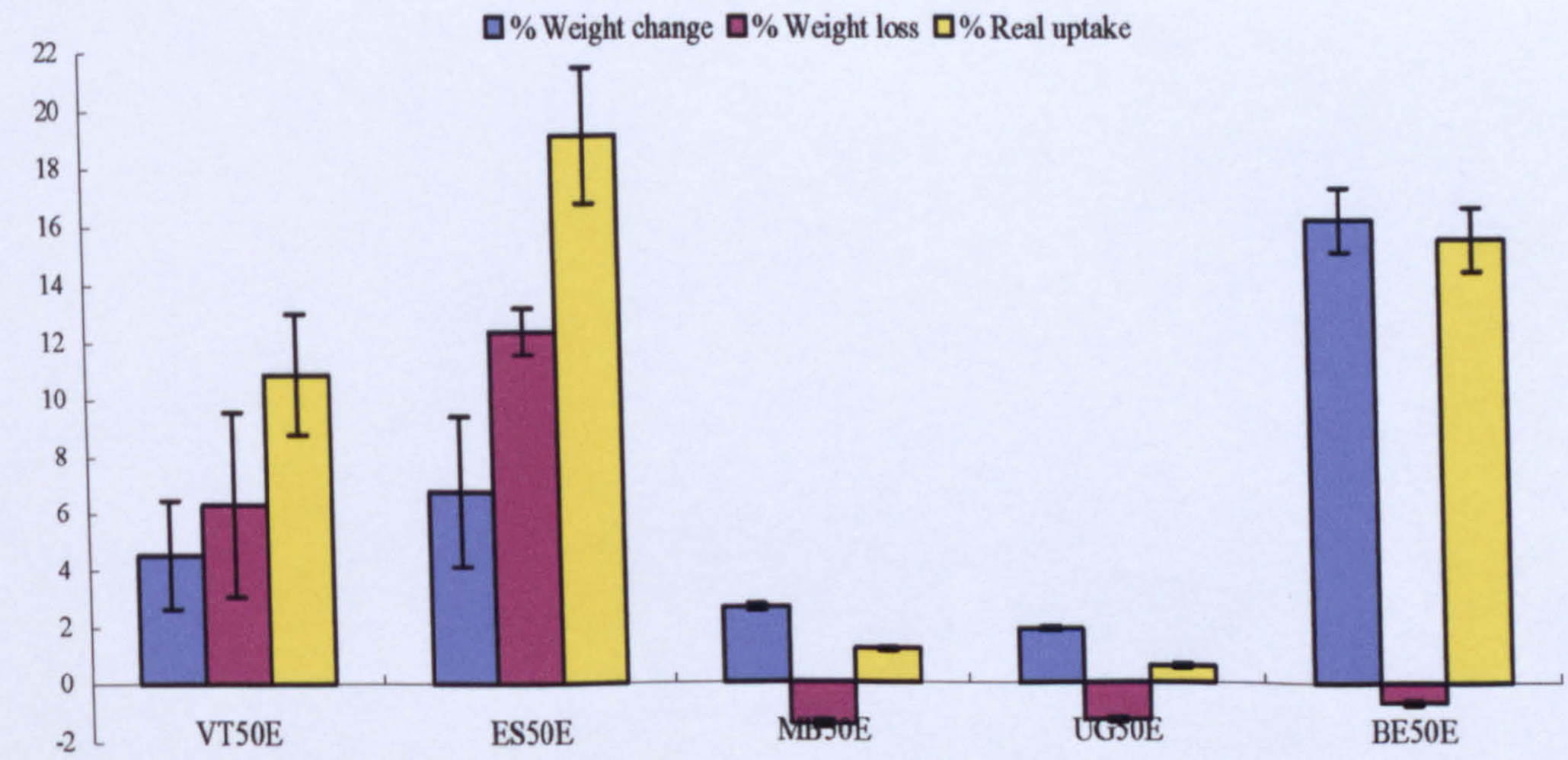


Figure 5.10 Bar chart of % weight change, weight loss, and real uptake of materials in 50% ethanol at one year.

5.1.1.6 Fluid uptake of specimens stored in coconut oil

Table 5.6 Summary of the fluid uptake of materials after one year storage in coconut oil (no change of solution), mean (sd), (n=6)

Materials	% Weight change /CO	% Weight loss /CO	% Real uptake /CO	Diffusion coefficient D_{abs} (10^{-13} m^2sec^{-1})
Vertex™Soft	-15.25 (0.10)	15.19 (0.20)	-0.06 (0.03)	*
EverSoft®	-23.90 (0.37)	25.21 (0.35)	1.31 (0.04)	*
Molloplast-B®	0.69 (0.21)	-0.20 (0.08)	0.47 (0.17)	227.29
Ufi Gel SC	1.05 (0.04)	-0.71 (0.04)	0.34 (0.02)	276.07
BE	173.70 (1.80)	-141.94 (12.41)	31.77 (12.61)	*

* Diffusion coefficient for Vertex™Soft, EverSoft® and BE could not be determined since no equilibrium had been reached.

Table 5.6 exhibits that VT and ES showed a weight loss but BE, MB and UG exhibited a weight increase. The change in weight of each material differed significantly from the others tested ($p<0.05$), the ranking being BE > UG > MB > VT > ES.

Figure 5.11 shows the weight of BE increased rapidly for up to three weeks then slowly increased for up to two months and then remained nearly constant up to one year. However, it was not clear whether BE had reached equilibrium. Longer immersion would be needed to clarify this result. Figure 5.12 exhibits MB and UG increased in weight up to six hours and then slowly decreased in weight for seven days after which the weight remained unchanged for the remainder of the year. The weight of VT and ES showed a continuous decrease in weight without reaching equilibrium for the period of up to one year.

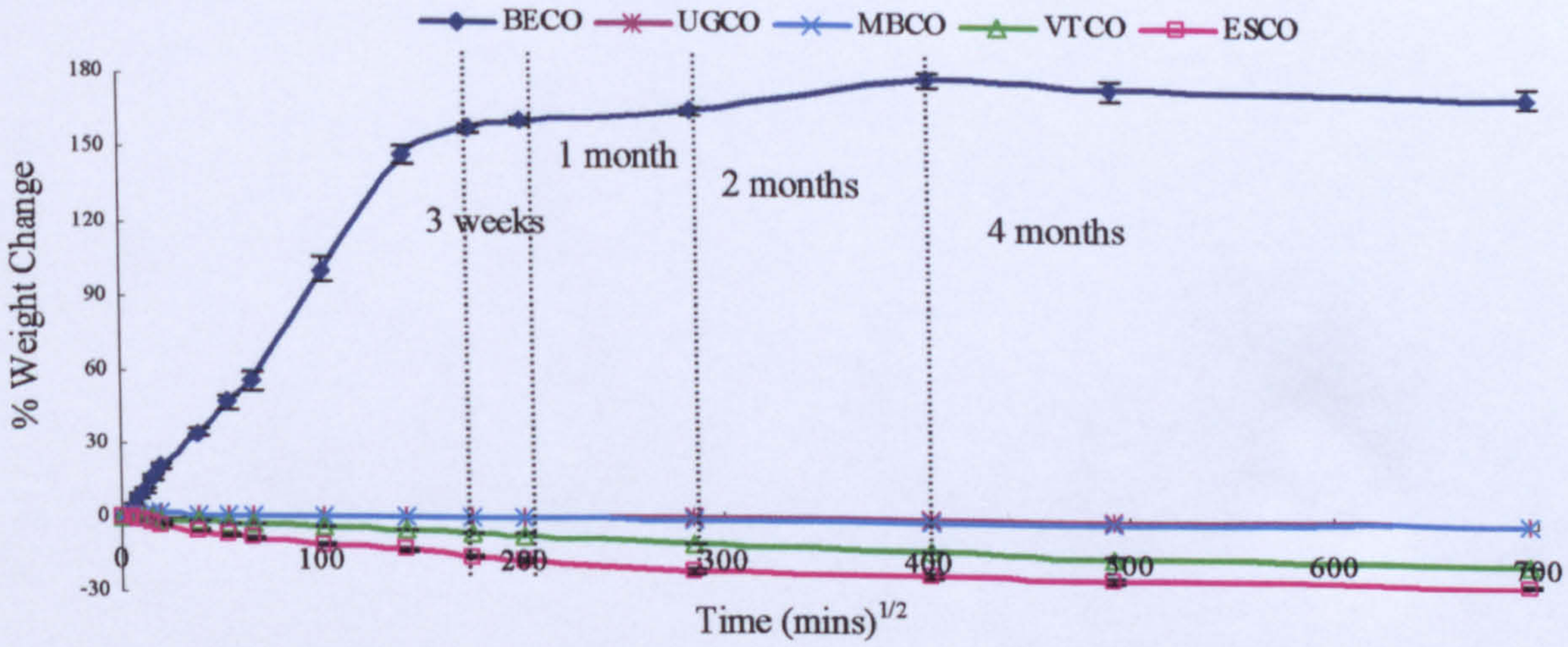


Figure 5.11 Mean percentage weight change of materials stored in coconut oil.

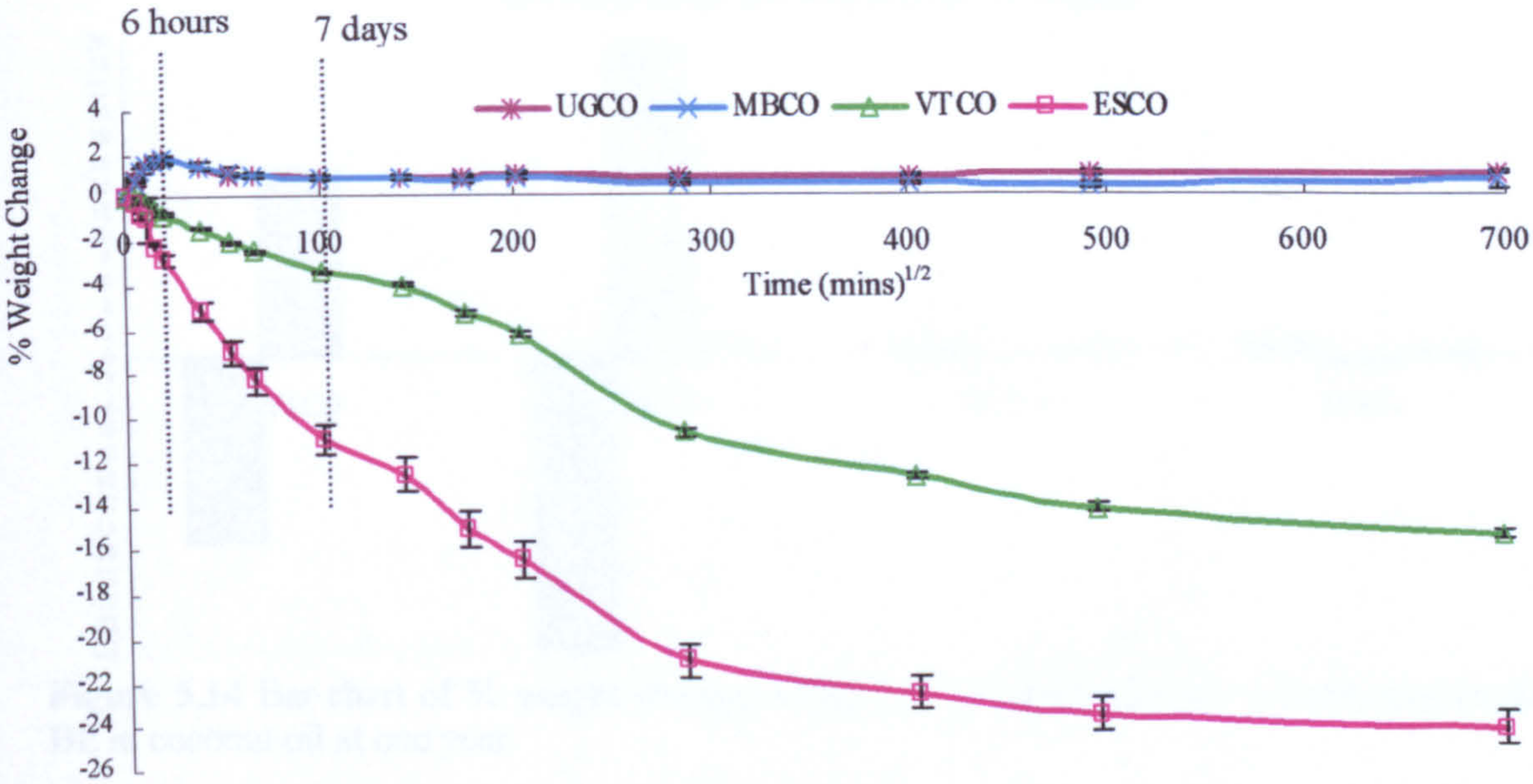


Figure 5.12 Mean percentage weight change of each materials excluding BE stored in coconut oil.

Figs 5.13-14 exhibit the percentage weight change, weight loss and real uptake in coconut oil at one year. For all materials the greatest change was observed with BE. A greater loss in weight was observed for ES and VT. There was no significant difference in percentage weight change between ES and VT, and between MB and UG ($P > 0.05$).

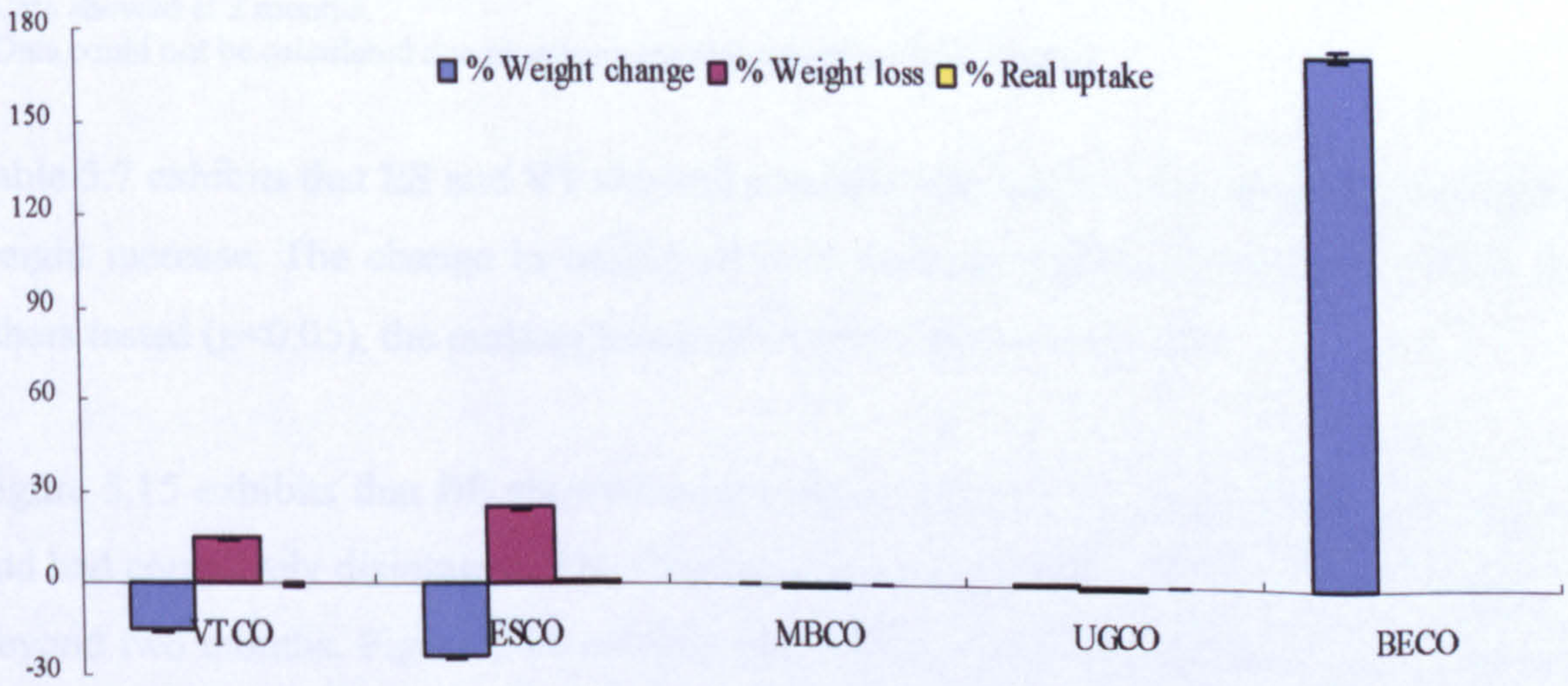


Figure 5.13 Bar chart of % weight change, weight loss, and real uptake of materials in coconut oil at one year.

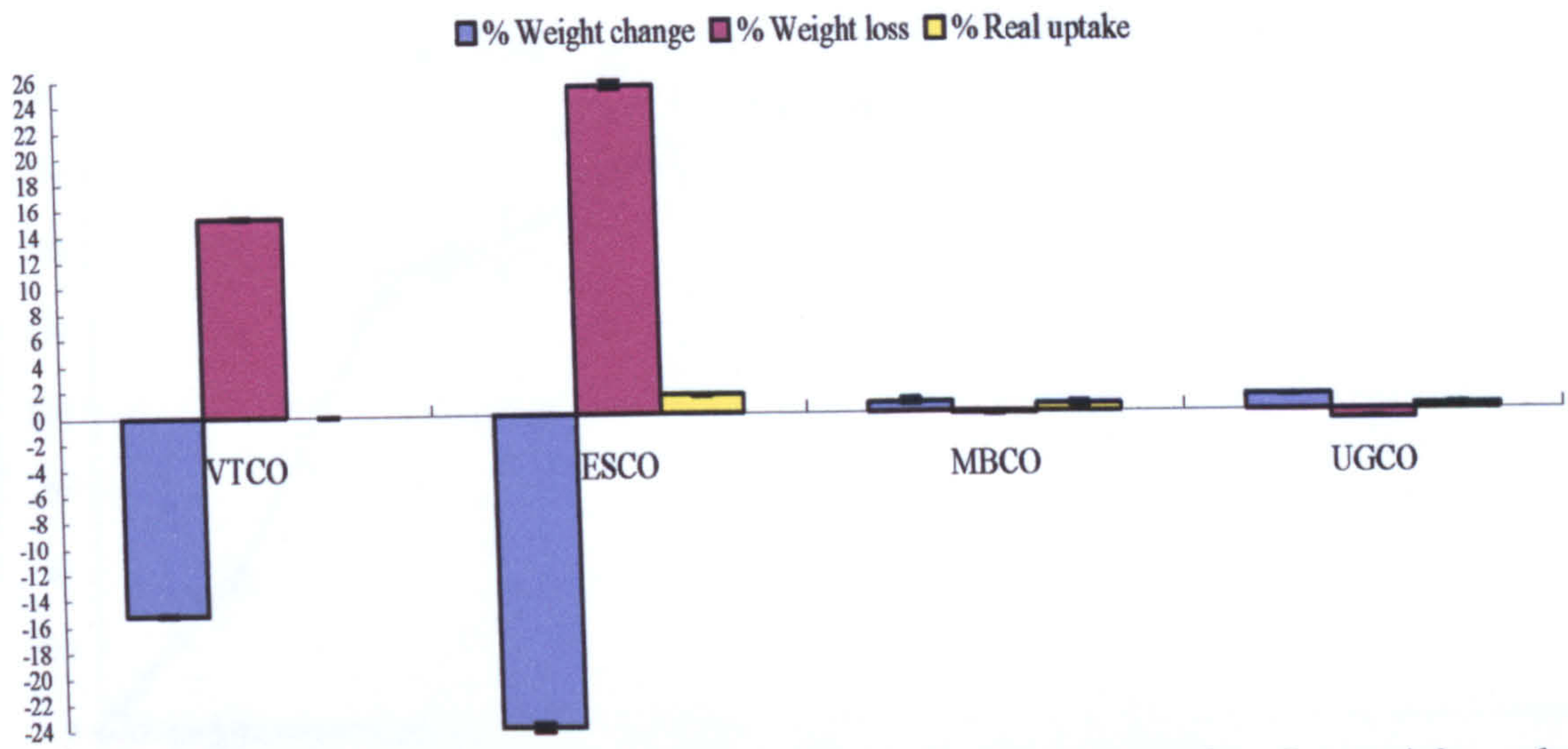


Figure 5.14 Bar chart of % weight change, weight loss, and real uptake of materials excluding BE in coconut oil at one year.

5.1.1.7 Fluid uptake of specimens stored in HB307

Table 5.7 Summary of the fluid uptake of materials after one year storage in HB307 (no change of solution), mean (sd), (n=6)

Materials	% Weight change /HB	% Weight loss /HB	% Real uptake /HB	Diffusion coefficient D_{abs} (10^{-13} m^2sec^{-1})
Vertex™Soft	-14.97 (0.23)	14.85 (0.24)	-0.12 (0.01)	*
EverSoft®	-23.96 (0.28)	25.22 (0.27)	1.25 (0.04)	*
Molloplast-B®	0.28 (0.13)	-0.16 (0.15)	0.12 (0.03)	290.38
Ufi Gel SC	0.39 (0.12)	-0.25 (0.09)	0.14 (0.22)	329.88
BE	†215.80 (10.0)	‡	‡	‡

* Diffusion coefficient for VT, ES and BE could not be determined since no equilibrium had been reached.
† Data showed at 2 months.
‡ Data could not be calculated due to specimens disintegrating by 4 months.

Table 5.7 exhibits that ES and VT showed a weight loss but BE, UG and MB exhibited a weight increase. The change in weight of each material differed significantly from the others tested ($p<0.05$), the ranking being BE > UG > MB > VT > ES.

Figure 5.15 exhibits that BE showed a continuous increase in weight up to two months and had completely disintegrated by four months so it was not possible to extend the data beyond two months. Figure 5.16 exhibits that MB and UG showed an initial increase to six hours and subsequently the weight decreased for seven days. After this time the weight remained unchanged for the remainder of time. VT and ES specimens showed a continuous decrease in weight without reaching equilibrium for the test period.

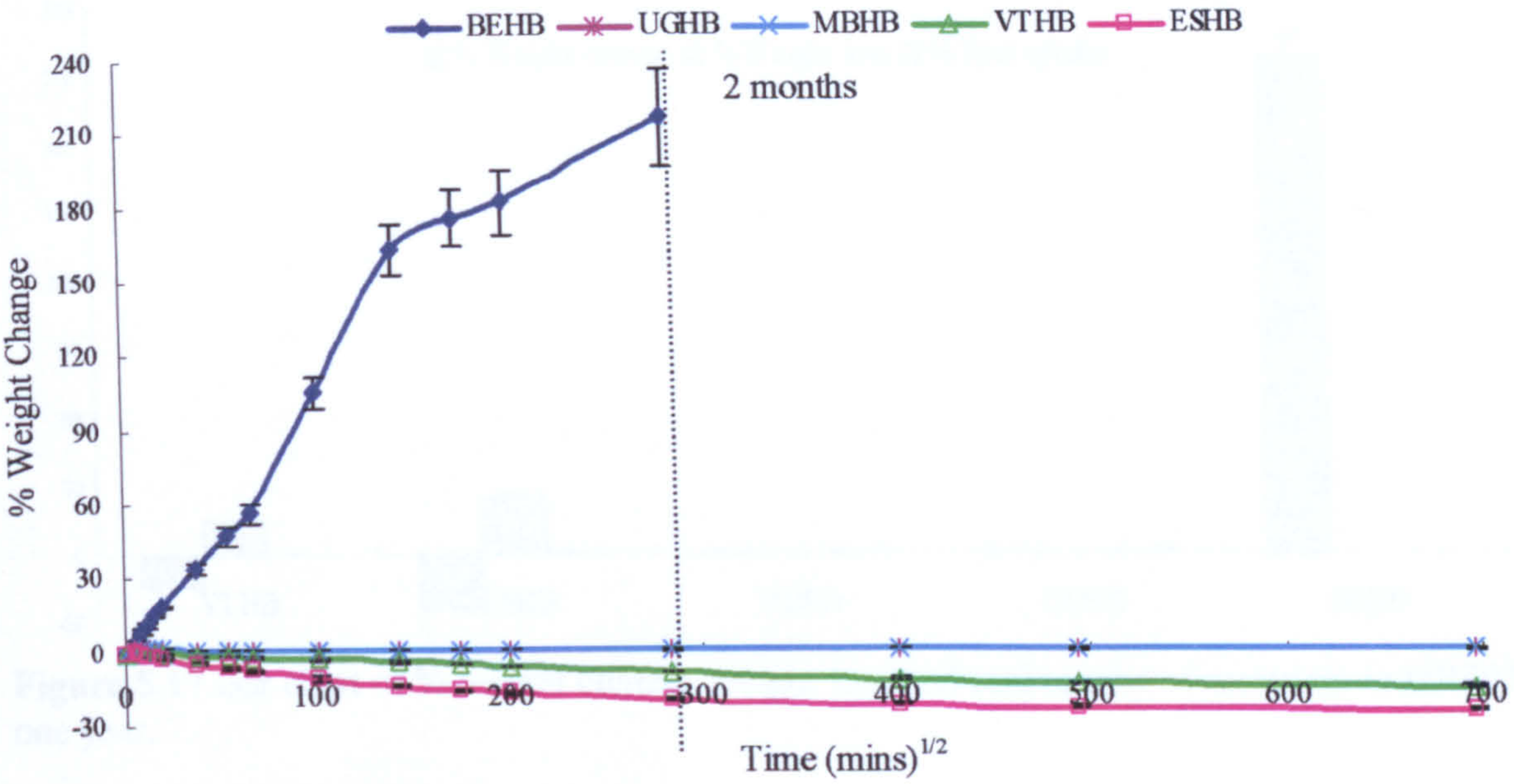


Figure 5.15 Mean percentage weight change of materials stored in HB307.

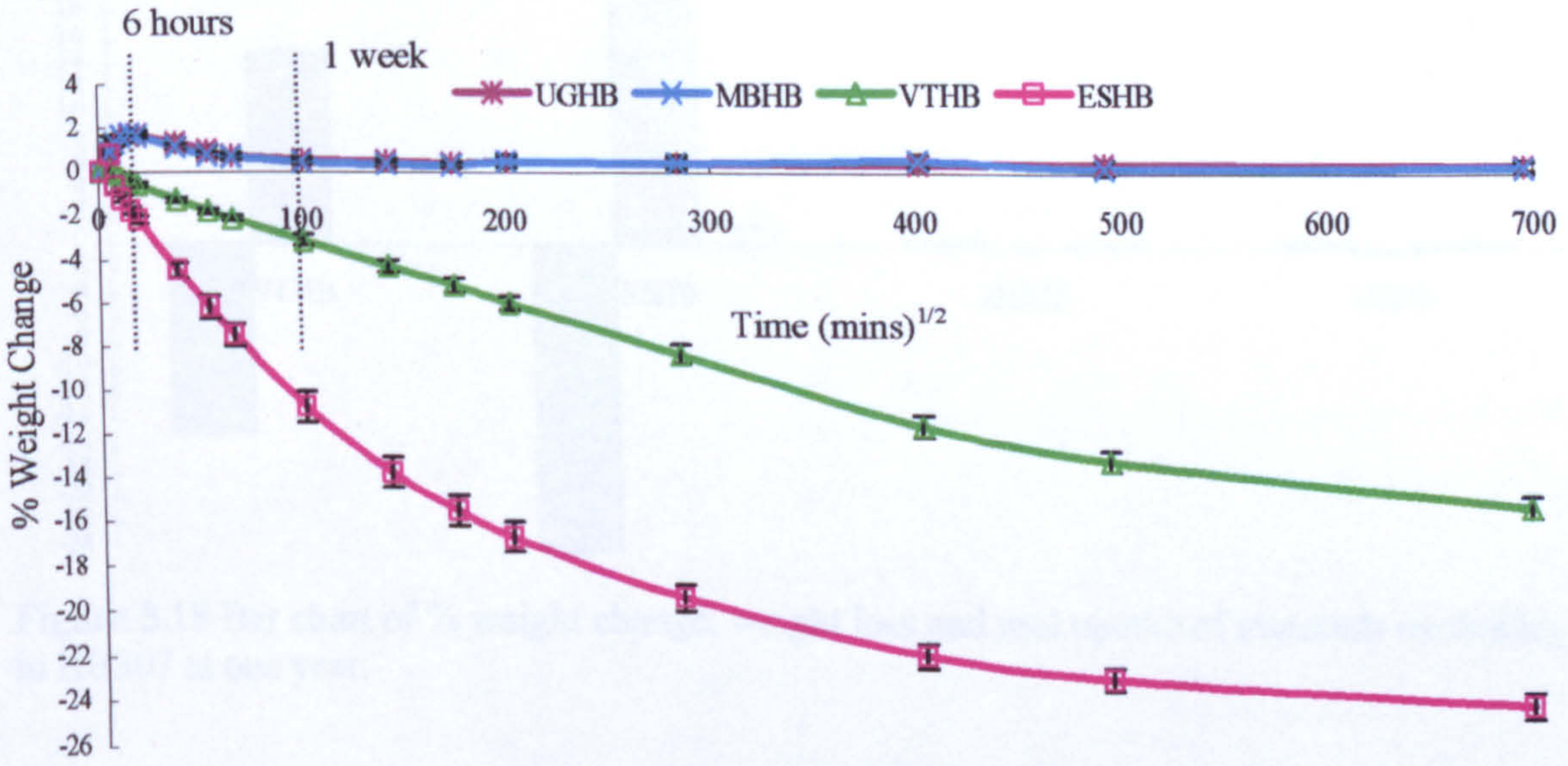


Figure 5.16 Mean percentage weight change of materials excluding BE stored in HB307.

Figs 5.17-18 show the percentage weight change, weight loss and real uptake in HB307 at one year. The greatest weight change was observed with BE. A greater loss in weight was observed for ES and VT. No significant difference was observed in percentage weight change between ES and VT, and between MB and UG ($P > 0.05$).

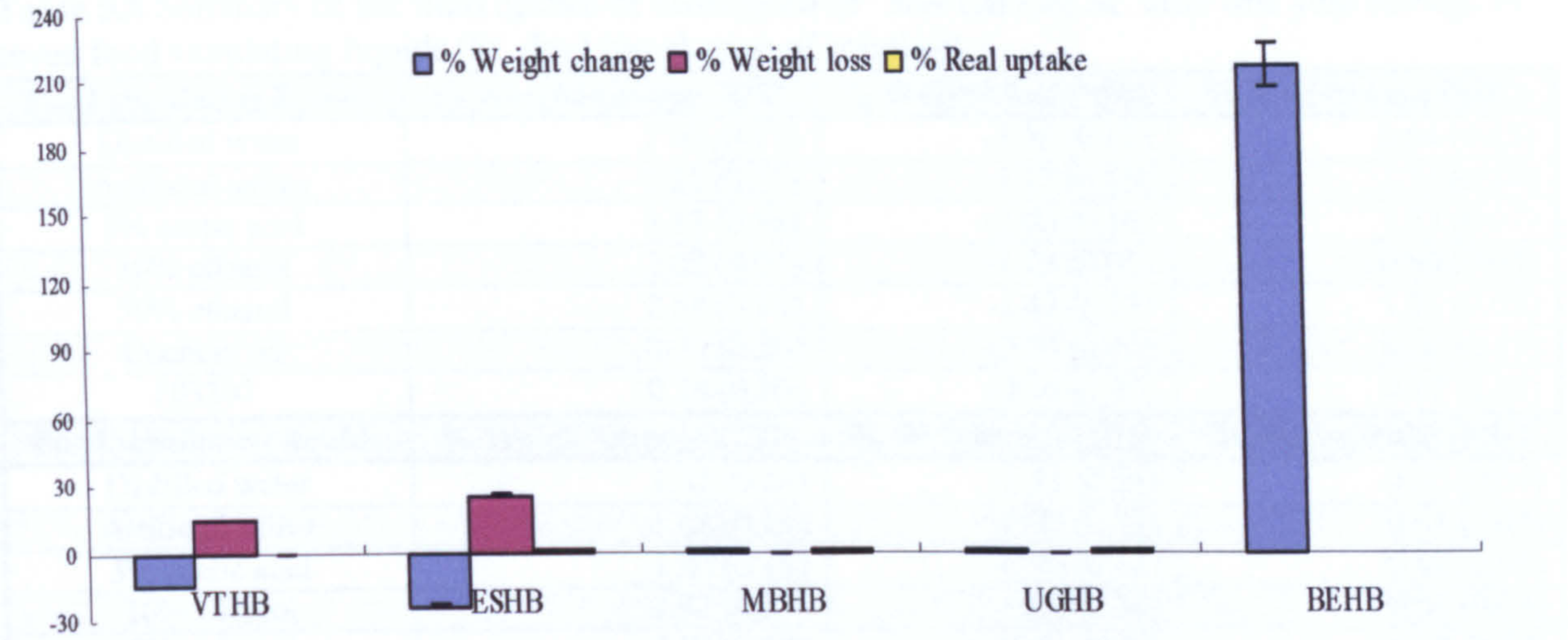


Figure 5.17 Bar chart of % weight change, weight loss and real uptake of materials in HB307 at one year.

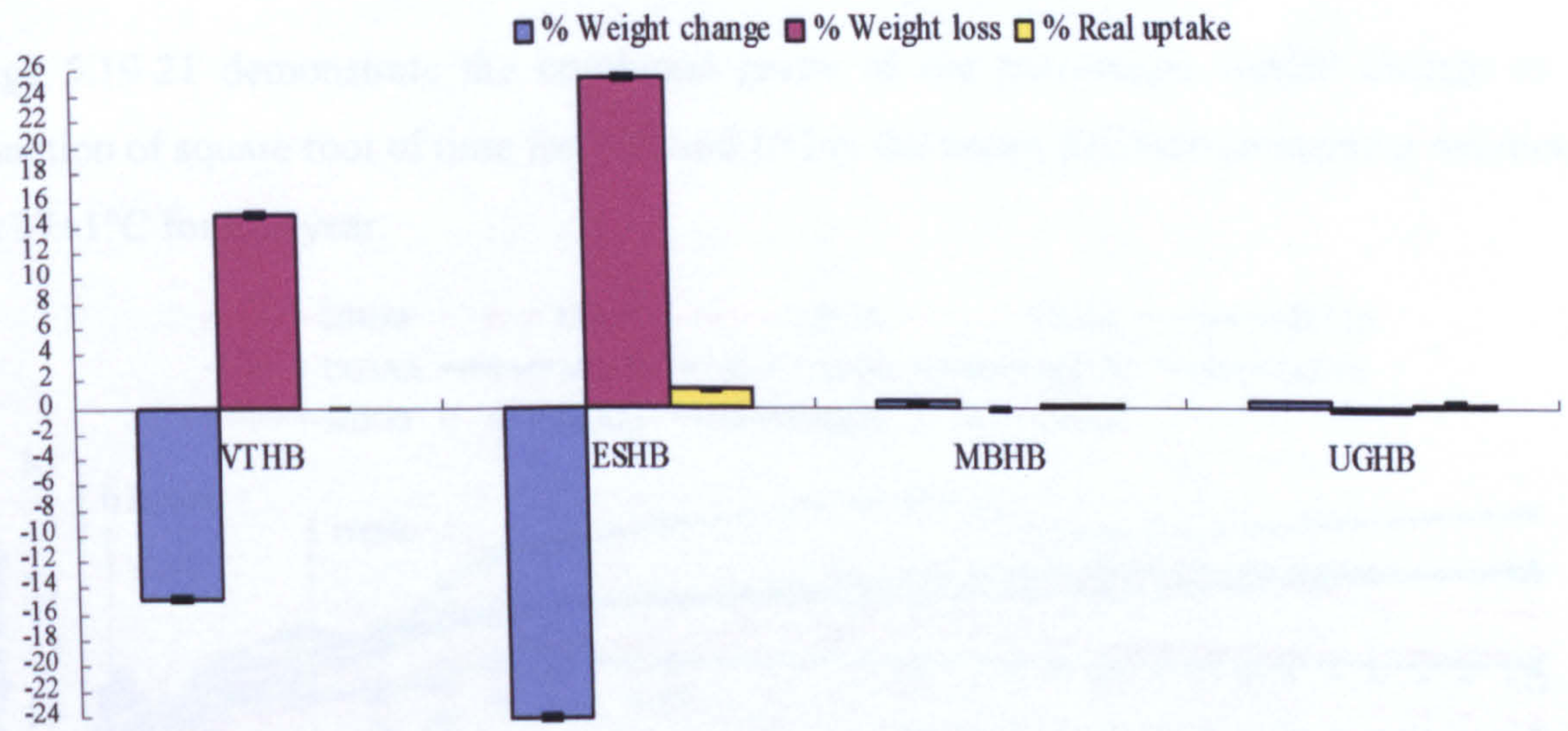


Figure 5.18 Bar chart of % weight change, weight loss and real uptake of materials excluding BE in HB307 at one year.

5.1.1.8 Summary of the unchanged solutions by generic type

Before considering the results for the changed solution, the results for this part of the study may be summarized by material type.

5.1.1.8.1 Silicone-based denture soft lining materials

Table 5.8 shows the combined summary of percentage weight change, weight loss and real fluid uptake of MB and UG in seven food simulating liquids after one year storage at 37±1°C.

Table 5.8 Summary of the fluid uptake of Molloplast-B® and Ufi Gel SC after one year storage in seven food simulating liquids (St. dev) (no change of solution)

Food simulating liquids	% Weight change (MB)	% Weight loss (MB)	% Real uptake (MB)
Distilled water	2.00 (0.11)	-1.36 (0.12)	0.64 (0.05)
Artificial saliva	2.31 (0.21)	-1.17 (0.15)	1.14 (0.14)
3% acetic acid	3.13 (0.16)	-2.00 (0.16)	1.13 (0.07)
10% ethanol	2.62 (0.03)	-1.73 (0.06)	0.89 (0.04)
50% ethanol	2.68 (0.14)	-1.47 (0.15)	1.21 (0.05)
Coconut oil	0.70 (0.20)	-0.20 (0.20)	0.50 (0.17)
HB307	0.28 (0.10)	-0.16 (0.20)	0.12 (0.03)
Food simulating liquids	**% Weight change (UG)**	**% Weight loss (UG)**	**% Real uptake (UG)**
Distilled water	1.92 (0.24)	-1.43 (0.24)	0.50 (0.04)
Artificial saliva	1.48 (0.15)	-0.80 (0.13)	0.68 (0.03)
3% acetic acid	1.80 (0.18)	-0.92 (0.18)	0.88 (0.08)
10% ethanol	1.37 (0.23)	-0.86 (0.26)	0.51 (0.03)
50% ethanol	1.94 (0.08)	-1.32 (0.09)	0.62 (0.08)
Coconut oil	1.05 (0.04)	-0.71 (0.04)	0.34 (0.02)
HB307	0.39 (0.12)	-0.25 (0.10)	0.14 (0.22)

Figs 5.19-21 demonstrate the combined graph of the percentage weight change as a function of square root of time for MB and UG in the seven different immersing solutions at 37±1°C for one year.

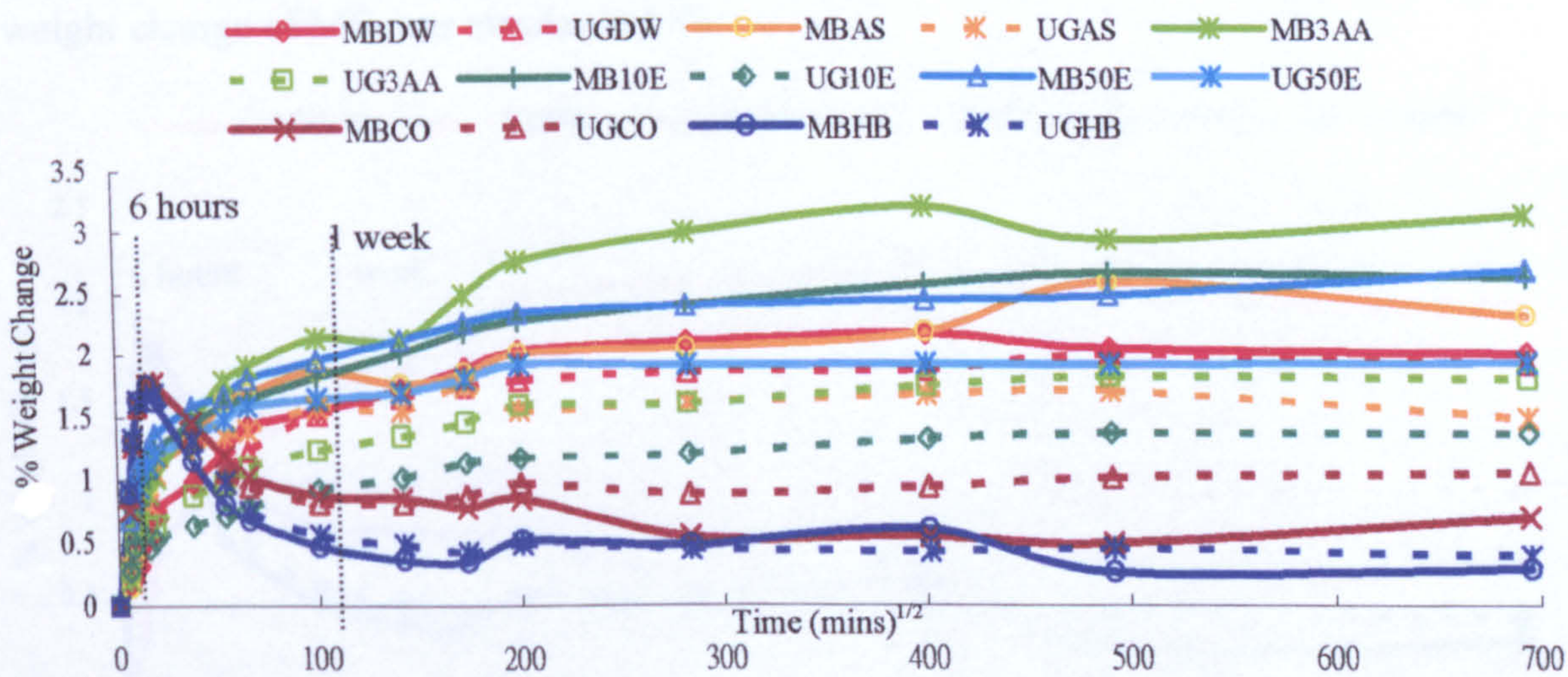


Figure 5.19 Combined graph demonstrates the percentage weight change as a function of square root of time for Molloplast-B® and Ufi Gel SC in the seven food simulating liquids at 37±1°C for one year.

In Figs 5.19-20, the specimens showed similar profiles in distilled water, artificial saliva, 3% acetic acid, 10% ethanol, and 50% ethanol. The specimens appeared to reach equilibrium at one month. UG was similar to the values observed for MB.

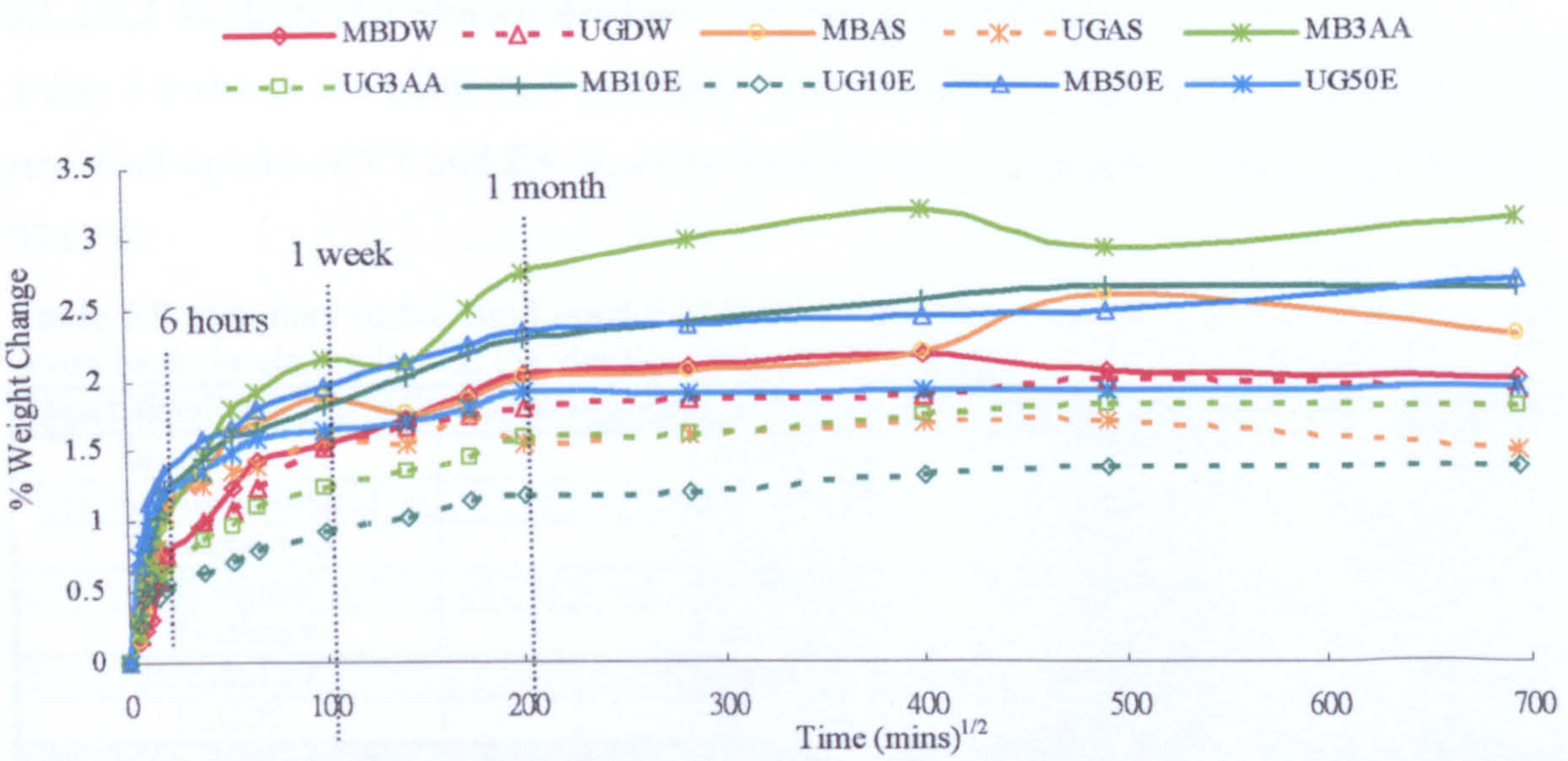


Figure 5.20 Expanded combined graph demonstrates the percentage weight change as a function of square root of time for Molloplast-B® and Ufi Gel SC in distilled water, artificial saliva, 3% acetic acid, 10% ethanol and 50% ethanol at 37±1°C for one year.

In Figure 5.21, the specimens in coconut oil and HB307 showed an initial rapid increase in weight, followed by a slow weight loss, finally appeared to reach equilibrium. The weight change of MB was similar to UG.

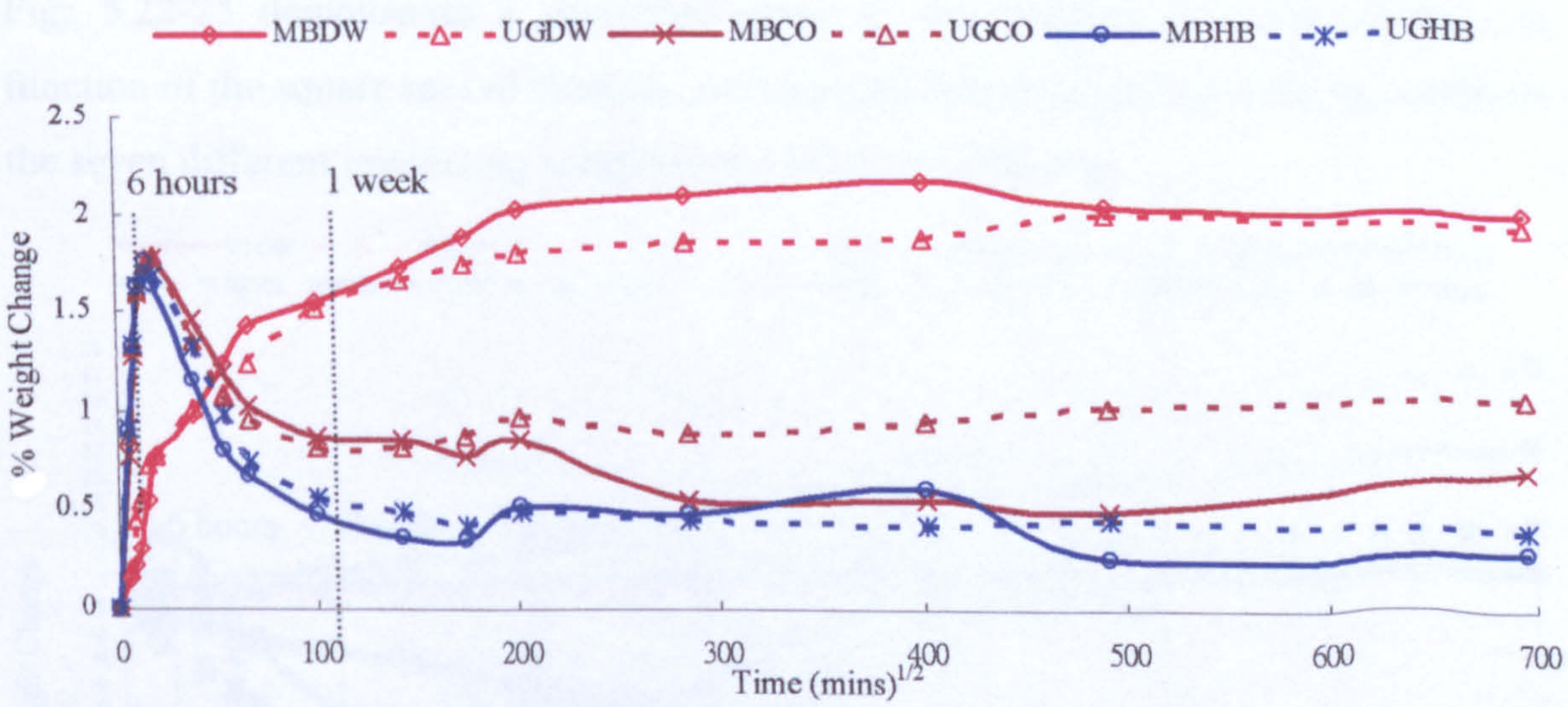


Figure 5.21 Expanded combined graph demonstrates the percentage weight change as a function of square root of time for Molloplast-B® and Ufi Gel SC in distilled water, coconut oil, and HB307 at 37±1°C for one year.

The cold-cured addition type UG and heat-cured MB silicone-based denture soft lining materials primarily showed little general change.

5.1.1.8.2 Methacrylate-based denture soft lining materials

Table 5.9 shows the combined summary of percentage weight change, weight loss and real fluid uptake of VT and ES, in seven food simulating liquids after one year storage at 37±1°C.

Table 5.9 Summary of the fluid uptake of Vertex™Soft and EverSoft® after one year storage in seven food simulating liquids (St. dev) (no change of solution)

Food simulating liquids	% Weight change (VT)	% Weight loss (VT)	% Real uptake (VT)
Distilled water	3.08 (0.39)	1.26 (0.12)	4.34 (0.39)
Artificial saliva	-2.94 (1.26)	7.93 (1.11)	4.99 (0.40)
3% acetic acid	13.10 (1.21)	1.51 (0.10)	14.61 (1.19)
10% ethanol	3.22 (0.22)	0.94 (0.24)	4.16 (0.13)
50% ethanol	4.58 (1.90)	6.33 (3.23)	10.90 (2.11)
Coconut oil	-15.25 (0.11)	15.19 (0.10)	-0.06 (0.03)
HB307	-14.97 (0.23)	14.85 (0.24)	-0.12 (0.01)
Food simulating liquids	**% Weight change (ES)**	**% Weight loss (ES)**	**% Real uptake (ES)**
Distilled water	4.83 (0.34)	13.45 (0.44)	18.28 (0.68)
Artificial saliva	-5.90 (0.63)	16.38 (0.45)	10.48 (0.47)
3% acetic acid	19.23 (1.39)	11.26 (0.75)	30.48 (1.84)
10% ethanol	6.95 (0.52)	13.48 (0.36)	20.43 (0.69)
50% ethanol	6.79 (2.64)	12.41 (0.81)	19.20 (2.37)
Coconut oil	-23.90 (0.37)	25.21 (1.31)	1.31 (0.04)
HB307	-23.96 (0.28)	25.22 (0.27)	1.26 (0.04)

Figs 5.22-25 demonstrate a combined graph of the percentage weight change as a function of the square root of time for methacrylate-based denture soft lining materials in the seven different immersing solutions at 37±1°C for one year.

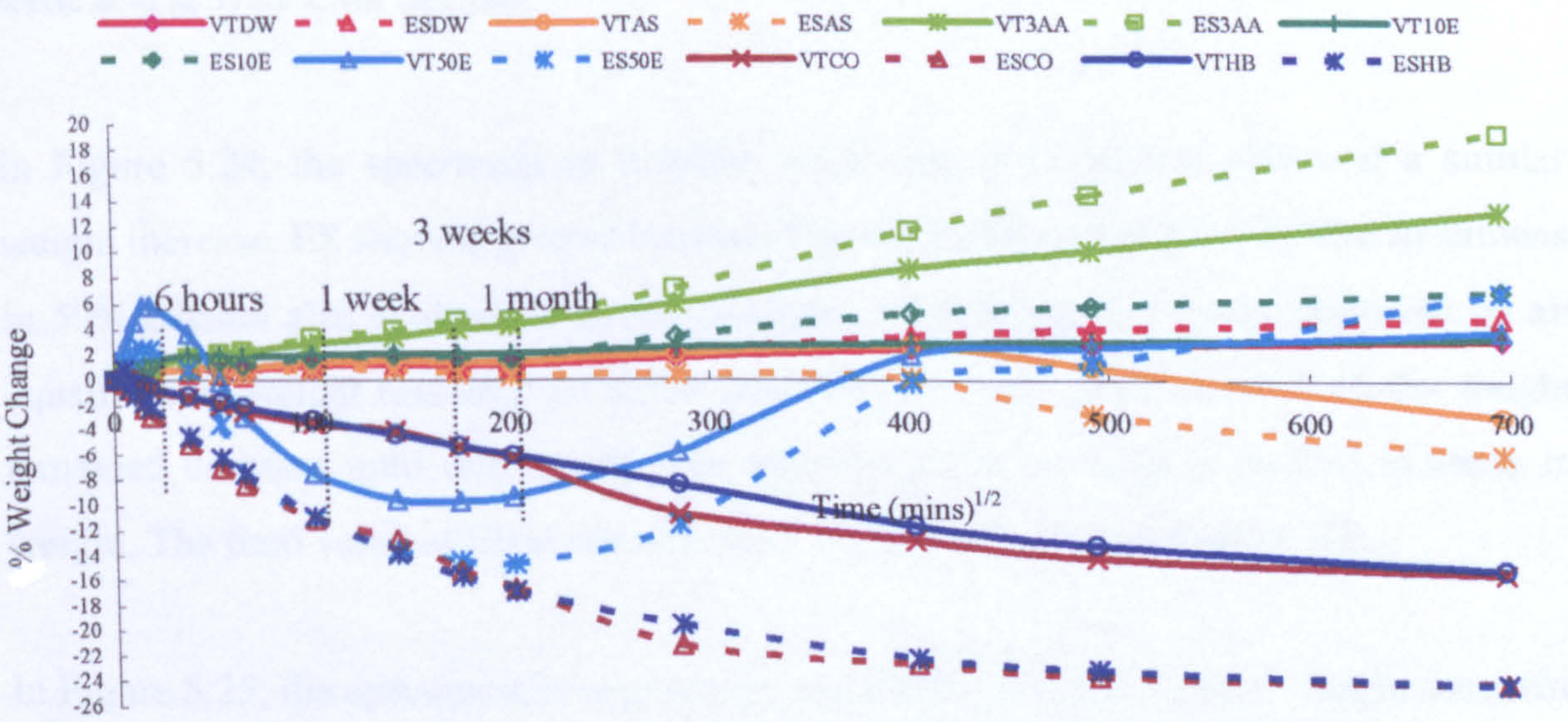


Figure 5.22 Combined graph demonstrates the percentage weight change as a function of square root of time for Vertex™Soft and EverSoft® in the seven food simulating liquids at 37±1°C for one year.

In Figure 5.23, the specimens in artificial saliva showed an increase in weight, followed by gradual weight loss, and finally achieved a net weight loss. The overall weight loss of ES was almost double than of VT. The specimens in 3% acetic acid showed a gradual increase in weight, over the test period and achieved the greatest weight increase. ES showed substantially greater increase than for VT.

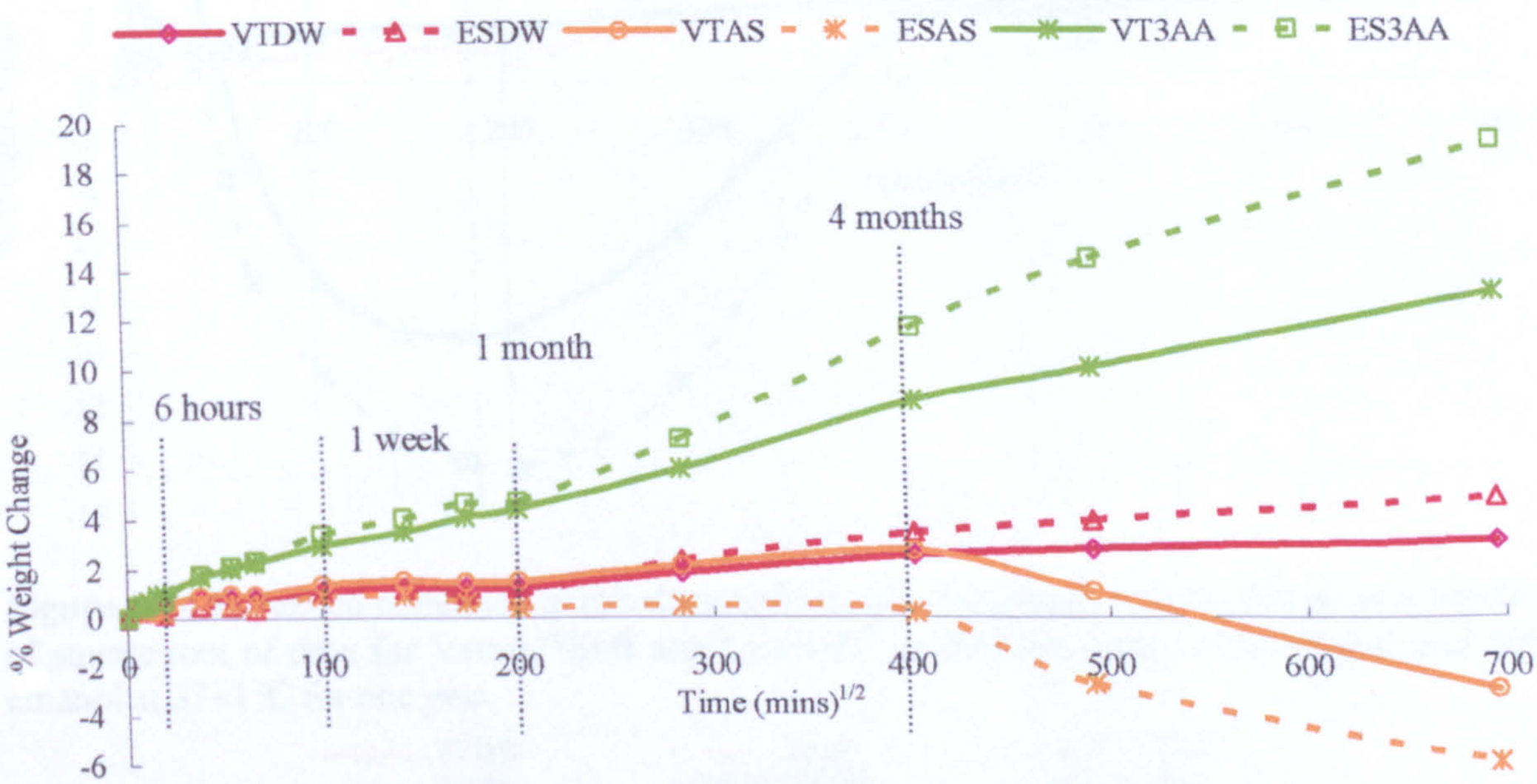


Figure 5.23 Expanded combined graph demonstrates the percentage weight change as a function of square root of time for Vertex™Soft and EverSoft® in distilled water, artificial saliva, and 3% acetic acid at 37±1°C for one year.

In Figure 5.24, the specimens in distilled water and 10% ethanol followed a similar weight increase. ES showed greater increase than the values noted for VT. The specimens in 50% ethanol also showed an initial increase in weight up to 6 hours, followed by an equally rapid weight loss until an immersion time of three weeks, after which the weight remained constant until one month. The specimens then showed a gradual increase in weight. The final value of ES at one year was slightly greater than that for VT.

In Figure 5.25, the specimens in coconut oil and HB307 showed a steady weight loss with respect to time, and finally achieved the greatest weight loss. The specimens exhibited

similar profiles in both oil solutions. Again, this weight change of ES was much greater than that observed for VT.

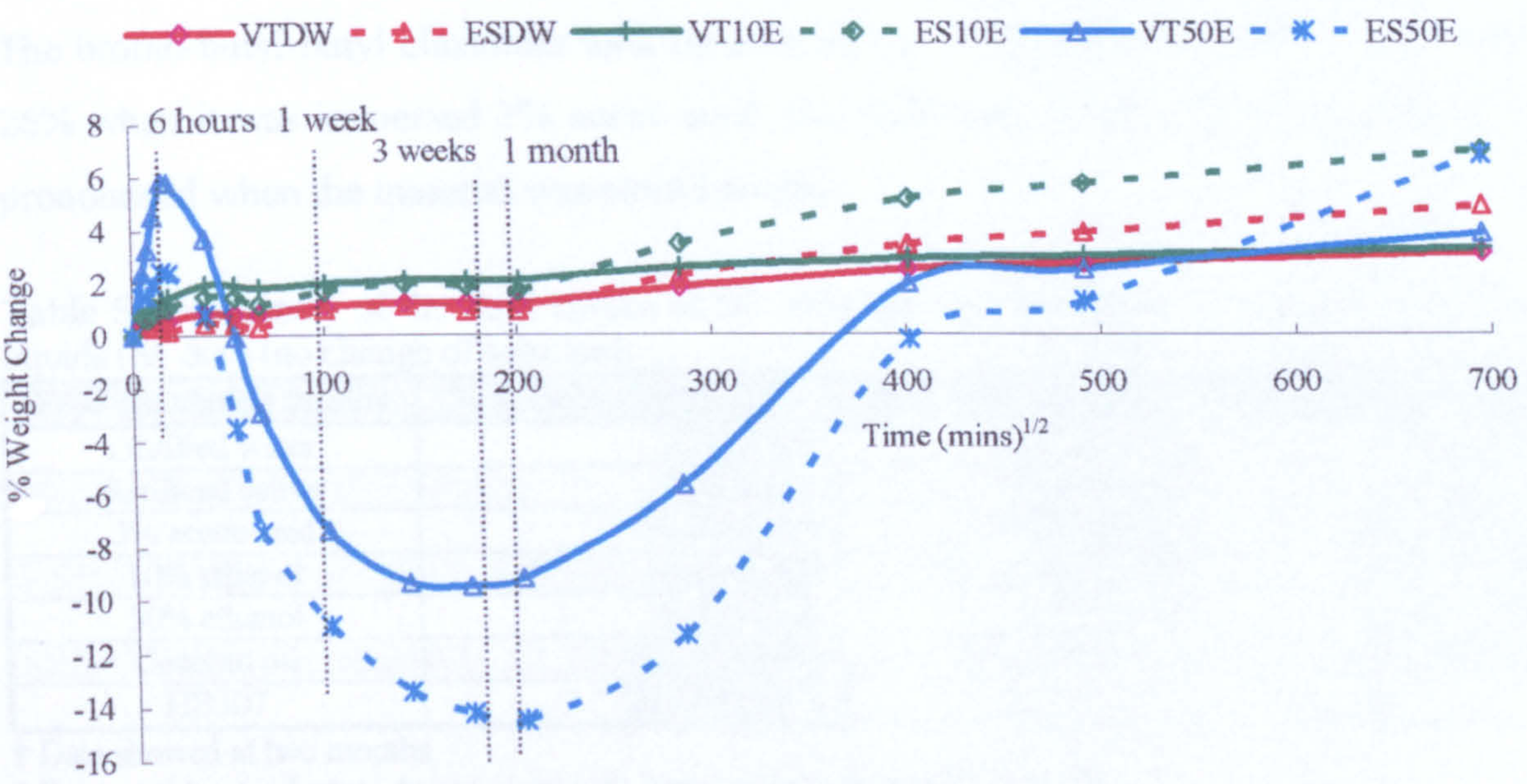


Figure 5.24 Expanded combined graph demonstrates the percentage weight change as a function of square root of time for Vertex™Soft and EverSoft® in distilled water, 10% ethanol, and 50% ethanol at 37±1°C for one year.

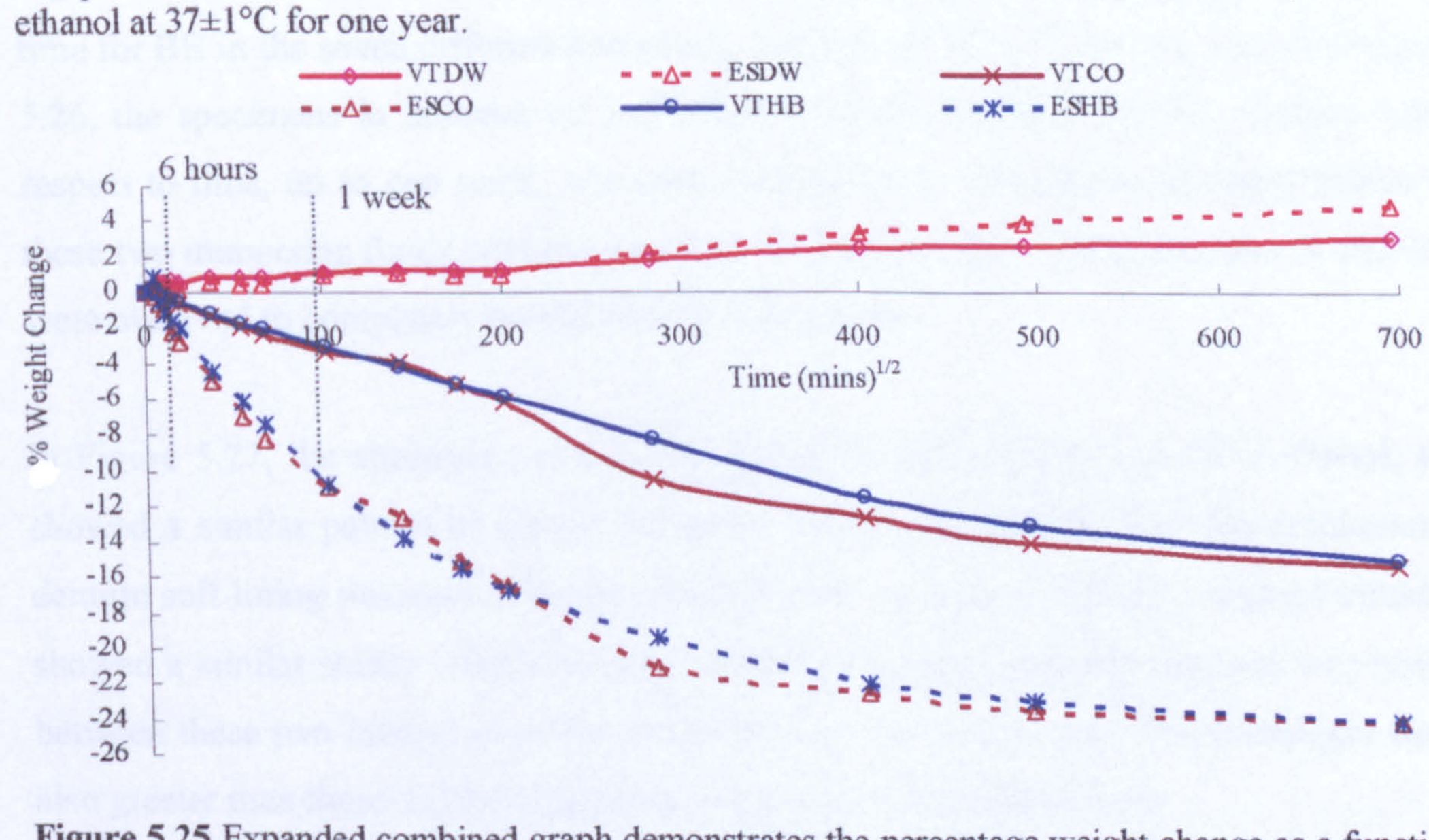


Figure 5.25 Expanded combined graph demonstrates the percentage weight change as a function of square root of time for Vertex™Soft and EverSoft® in distilled water, coconut oil, and HB307 at 37±1°C for one year.

5.1.1.8.3 Bromo-butyl butyl elastomer

Table 5.10 shows the combined summary of percentage weight change, weight loss and real fluid uptake of BE in seven food simulating liquids after one year storage at 37±1°C. The bromo-butyl butyl elastomer took up as much as 10% of water whereas it absorbed 26% when it was immersed 3% acetic acid. The fluid uptake and expansion were more pronounced when the material was stored in oils.

Table 5.10 Summary of the fluid uptake of BE after one year storage in seven food simulating liquids (St. dev) (no change of solution).

Food simulating liquids	% Weight change (BE)	% Weight loss (BE)	% Real uptake (BE)
Distilled water	9.71 (1.86)	-0.29 (0.13)	9.42 (1.86)
Artificial saliva	7.13 (1.32)	0.39 (0.40)	7.52 (1.02)
3% acetic acid	26.00 (1.21)	-0.25 (0.46)	25.75 (1.10)
10% ethanol	12.48 (1.14)	-0.30 (0.17)	12.19 (1.07)
50% ethanol	16.30 (1.11)	-0.67 (0.09)	15.63 (1.11)
Coconut oil	173.70 (1.80)	-141.94 (12.41)	31.77 (12.61)
HB307	†215.80 (10.0)	‡	‡

† Data showed at two months.
‡ Data could not calculate due to specimens had disintegrated by four months.

Figs 5.26-27 illustrate the percentage weight change as a function of the square root of time for BE in the seven different immersing solutions at 37±1°C for one year. In Figure 5.26, the specimens in coconut oil and HB307 showed a similar weight increase with respect to time, up to one week, but some divergence in behaviour was noted between these two immersing fluids between one week and two months. The specimens in HB307 were observed to completely breakdown by four months.

In Figure 5.27, the specimens in distilled water, artificial saliva, and 10% ethanol, all showed a similar pattern of weight increases. These were greater than the commercial denture soft lining materials. The specimens in 3% acetic acid and 50% ethanol initially showed a similar steady weight increase up to two months. Some divergence was noted between these two immersing fluids from four months to one year. These changes were also greater than those for the commercial denture soft lining materials.

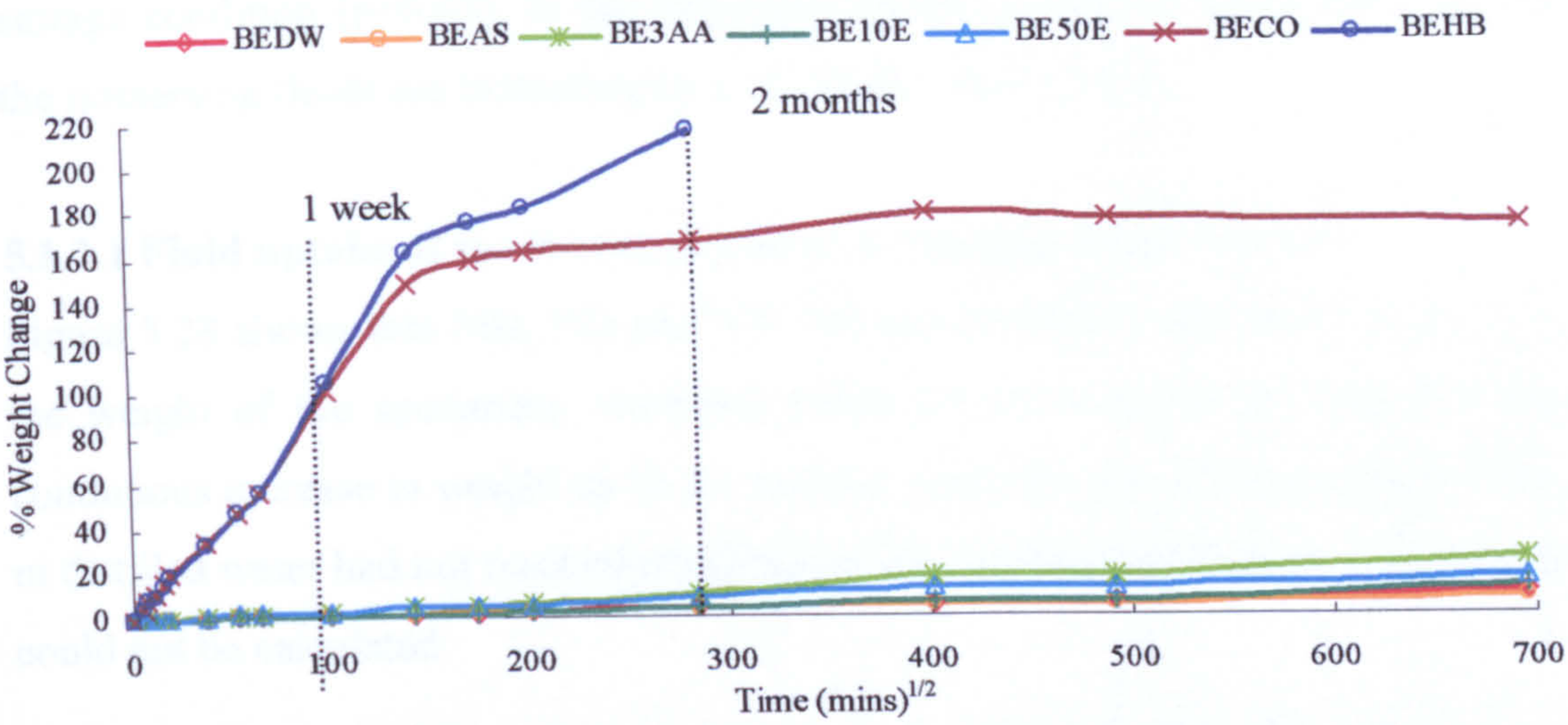


Figure 5.26 Combined graph demonstrates the percentage weight change as a function of square root of time for bromo-butyl butyl elastomer in the seven food simulating liquids at 37±1°C for one year.

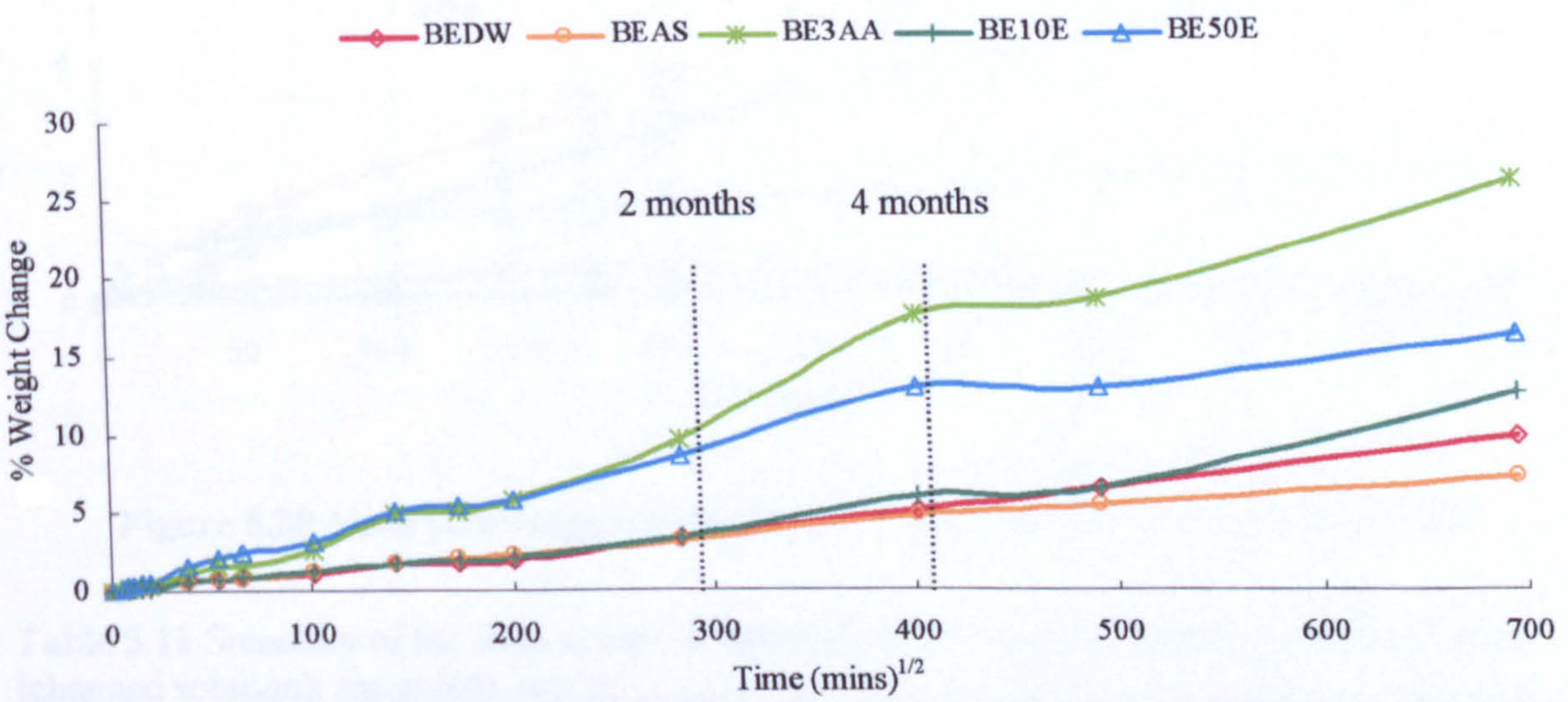


Figure 5.27 Combined graph demonstrates the percentage weight change as a function of square root of time for bromo-butyl butyl elastomer in the five food simulating liquids (excluding oils) at 37±1°C for one year.

5.1.2 Fluid uptake of specimens stored in a changed storage medium

Tables 5.11-15 show the percentage weight change, solubility and real fluid uptake of specimens in five changed food simulating liquids (excluding oils) after six months storage at 37±1°C. In this section the immersing fluids were changed throughout the study at predetermined intervals. The statistical analysis showed significant differences in percentage weight change, solubility, and real uptake with time for each material and

storage condition ($p<0.05$). In the following tables and figures the results for changing the immersing fluids are indicating by a 'C' in the abbreviation.

5.1.2.1 Fluid uptake of specimens stored in a changed distilled water

Figure 5.28 shows that MB, UG and VT had equilibrated within seven days. Thereafter the weight of the specimens remained stable for six months. ES and BE showed a continuous increase in weight up to six months. Since the specimens of ES and BE stored in distilled water had not reached equilibrium, the sorption parameters of these specimens could not be calculated.

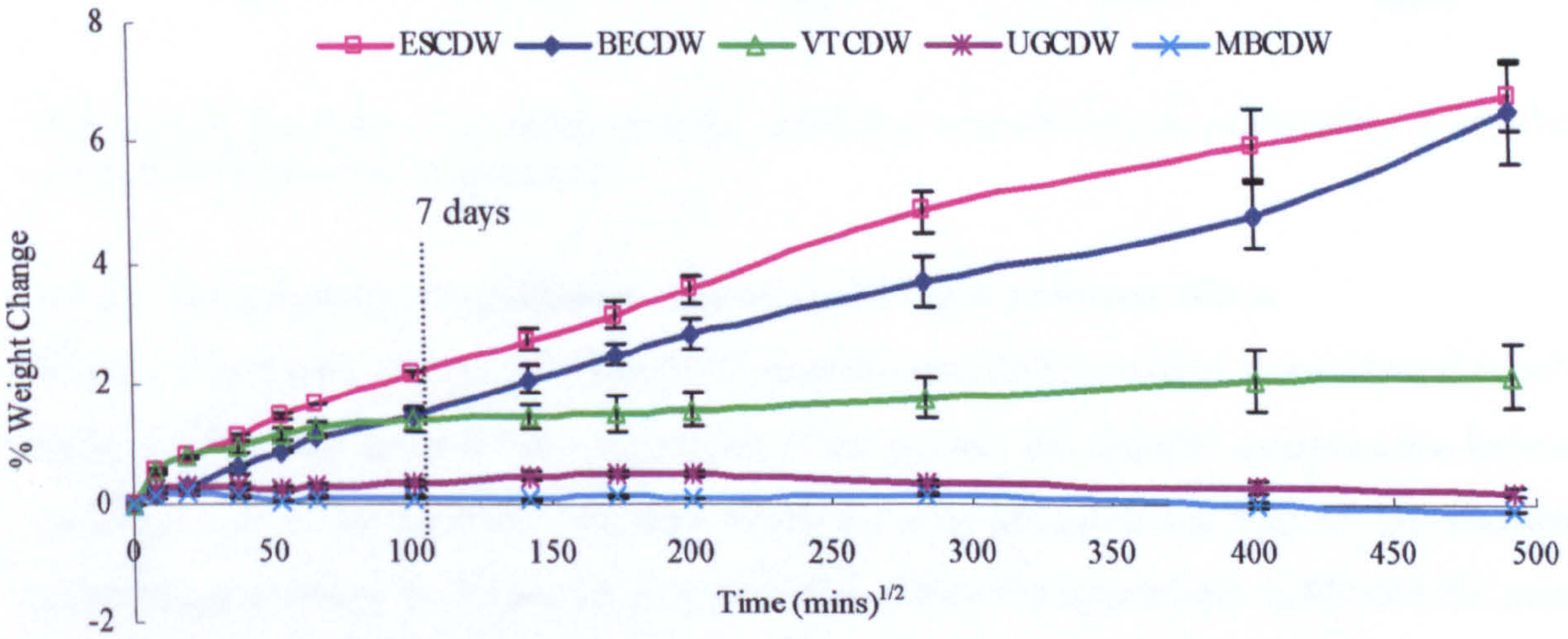


Figure 5.28 Mean percentage weight change of materials stored in the changed DW.

Table 5.11 Summary of the fluid uptake of materials after 6 months storage in distilled water (changed solution), mean (sd), (n=3).

Materials	% Weight change (CDW)	% Solubility (CDW)	% Real uptake (CDW)	Diffusion coefficient D_{abs} (10^{-13} m^2sec^{-1})
Vertex™Soft	2.14(0.54)	1.27(0.10)	3.41(0.54)	2.65
EverSoft®	6.75(0.56)	8.41(1.06)	15.16(1.62)	*
Molloplast-B®	-0.12(0.02)	0.50(0.10)	0.37(0.08)	3.14
Ufi Gel SC	0.19(0.08)	0.29(0.09)	0.48(0.11)	6.12
BE	6.47(0.85)	-0.70(0.09)	5.77(0.79)	*

* Diffusion coefficient for EverSoft® and BE could not be determined since no equilibrium had been reached.

Table 5.11 and Fig 5.29 show that the denture soft lining materials increased in weight by up to 6.8% in water while the BE increased by 6.5%. The weight gain for each material was ranked ES > BE > VT > UG > MB. No significant difference was observed between ES and BE, and between MB and UG ($p>0.05$). A greater solubility was observed with

ES and VT. Additionally, the real uptake of ES, BE and VT was significantly greater than for MB and UG ($p<0.05$).

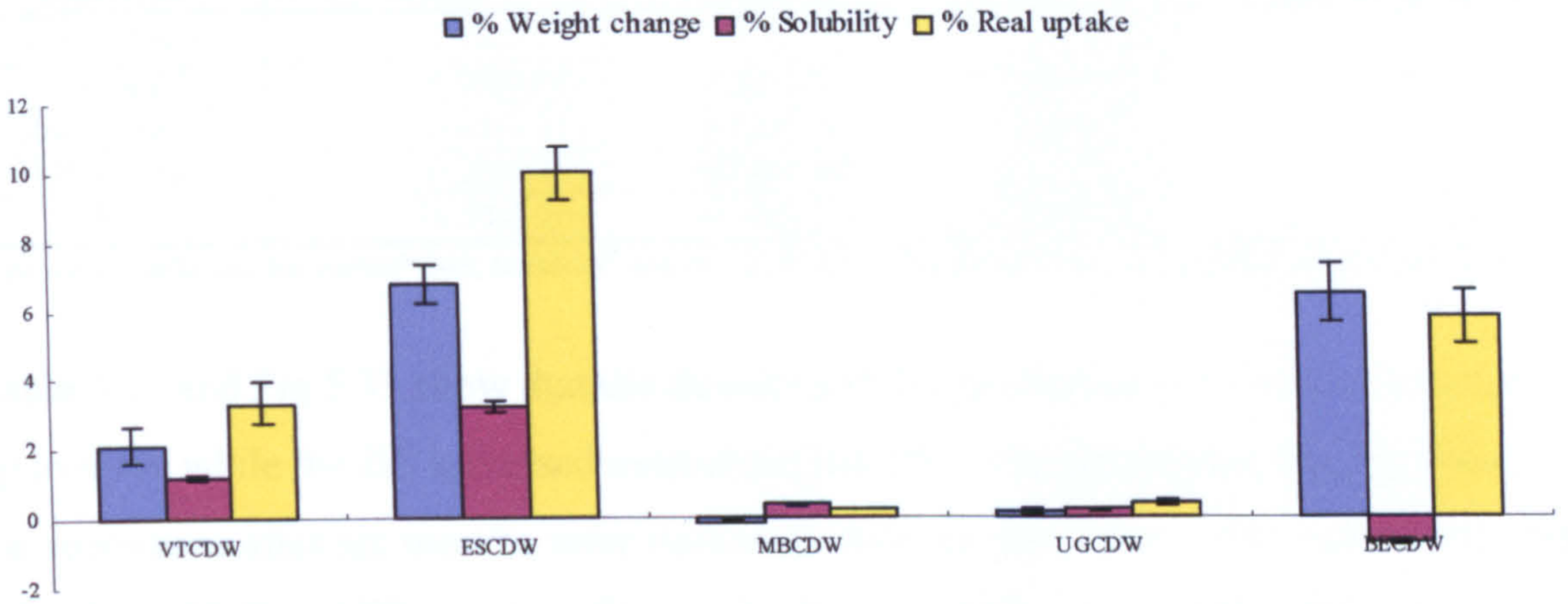


Figure 5.29 Bar chart of % weight change, solubility, and real uptake of materials in regularly changed distilled water at six months.

5.1.2.2 Fluid uptake of specimens stored in changed artificial saliva

Figure 5.30 shows that MB, UG and VT reached equilibrium within three days; thereafter little variation occurred for the remainder of the period. ES showed a continuous increase in weight up to three months and then remained constant up to six months. BE showed a continuous increase in weight up to six months. Since the specimens of ES and BE stored in changed artificial saliva had not reached equilibrium, the sorption parameters of these specimens could not be calculated.

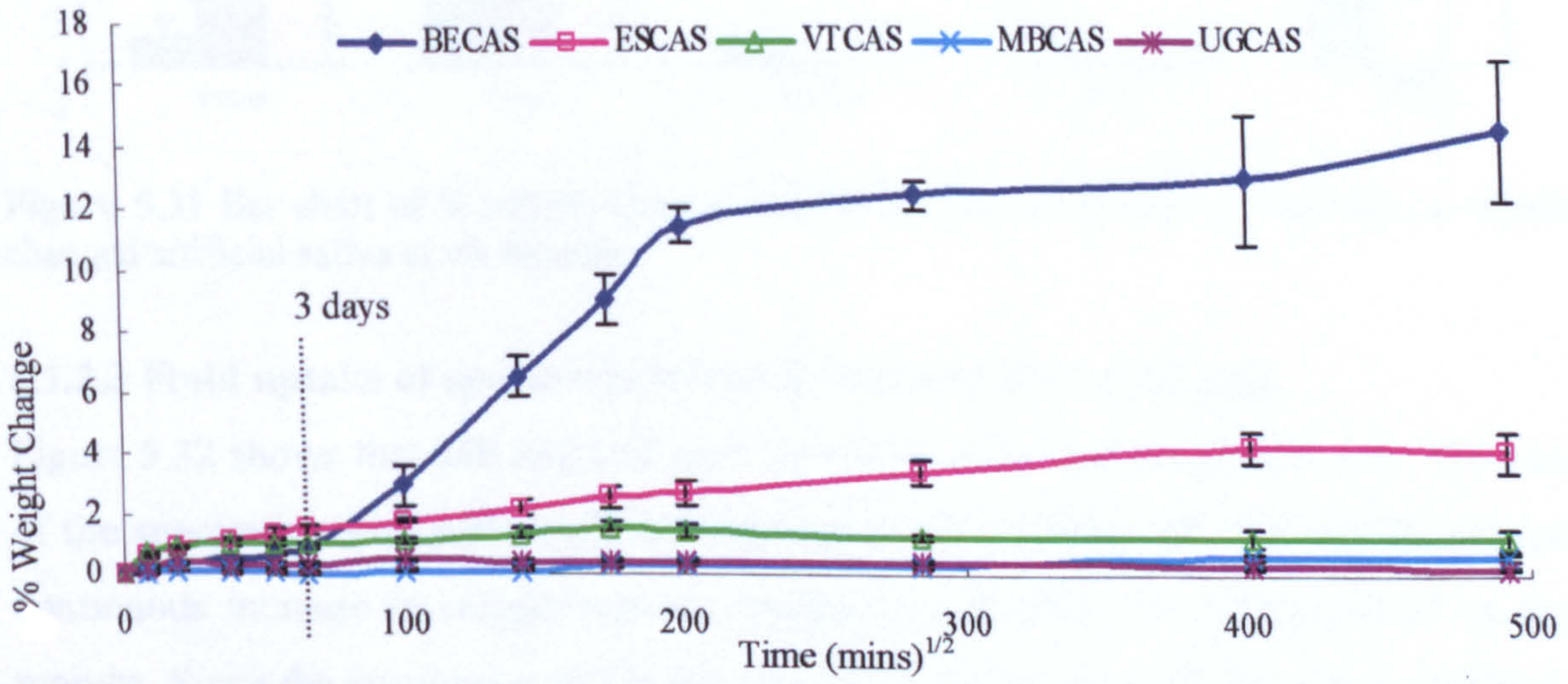


Figure 5.30 Mean percentage weight change of materials stored in changed artificial saliva.

Table 5.12 Summary of the fluid uptake of materials after 6 months storage in artificial saliva (changed solution), mean (sd), (n=3)

Materials	% Weight change /CAS	% Solubility /CAS	% Real uptake /CAS	Diffusion coefficient D_{abs} (10^{-13} m^2sec^{-1})
Vertex™Soft	1.22(0.70)	6.57(0.39)	7.79(0.09)	*
EverSoft®	4.09(0.66)	9.30(0.83)	13.38(1.17)	*
Molloplast-B®	0.65(0.11)	0.28(0.16)	0.93(0.07)	0.47
Ufi Gel SC	0.26(0.06)	0.45(0.04)	0.71(0.07)	3.28
BE	14.55(2.26)	-0.68(0.11)	13.87(2.35)	*

* Diffusion coefficient for Vertex™Soft, EverSoft® and BE could not be determined since no equilibrium had been reached.

Table 5.12 and Fig 5.31 show that the denture soft lining materials increased in weight by up to 4.1% while the BE increased even more (14.6%). The percentage weight changes of the specimens after six months were ranked as follows: BE > ES > VT > MB > UG. The solubility of VT and ES was significantly higher than MB, UG, and BE ($p<0.05$), and the ranking was ES > VT > UG > MB > BE. The real uptake of BE, ES and VT was significantly higher than MB and UG ($p<0.05$), and the ranking was BE > ES > VT > MB > UG.

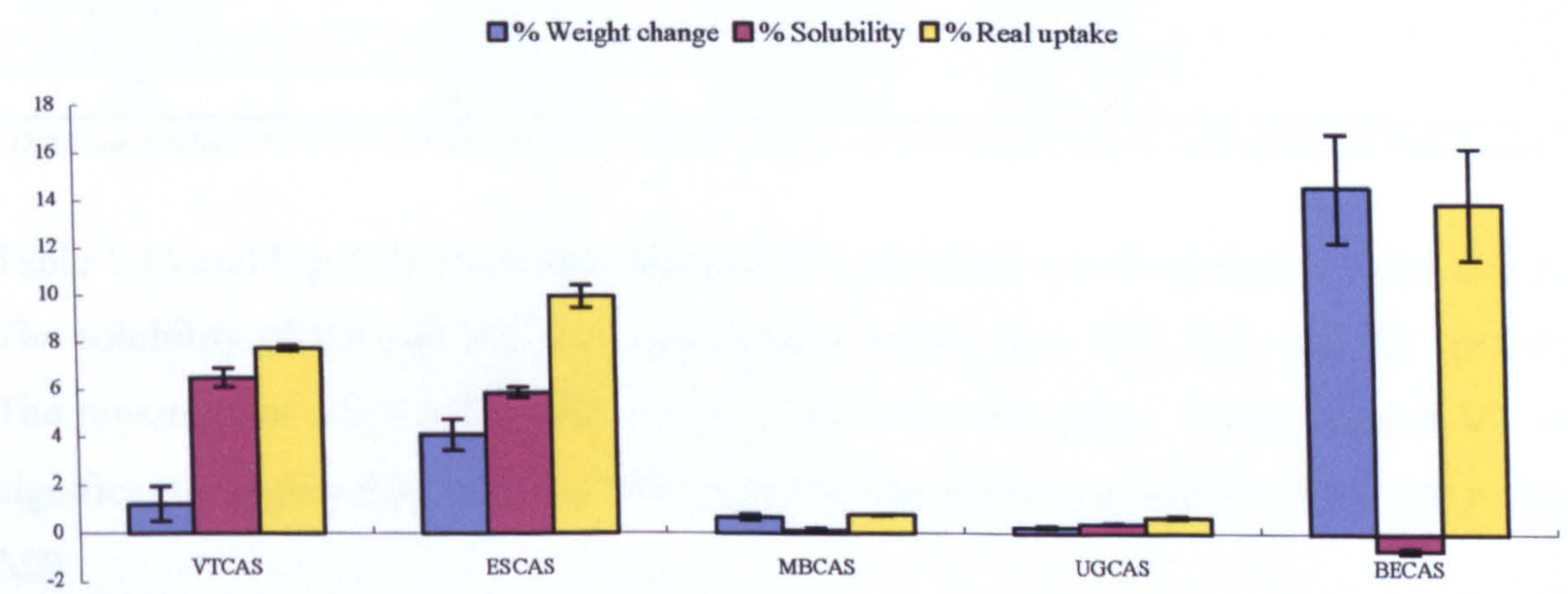


Figure 5.31 Bar chart of % weight change, solubility, and real uptake of materials in regularly changed artificial saliva at six months.

5.1.2.3 Fluid uptake of specimens stored in changed 3% acetic acid

Figure 5.32 shows that MB and UG were saturated with fluid within one day; the weight of the specimens remained nearly constant up to six months. VT, ES and BE showed a continuous increase in weight without reaching equilibrium for the period of up to six months. Since the specimens of VT, ES and BE stored in changed 3% acetic acid had not reached equilibrium, the sorption parameters of these specimens could not be calculated.

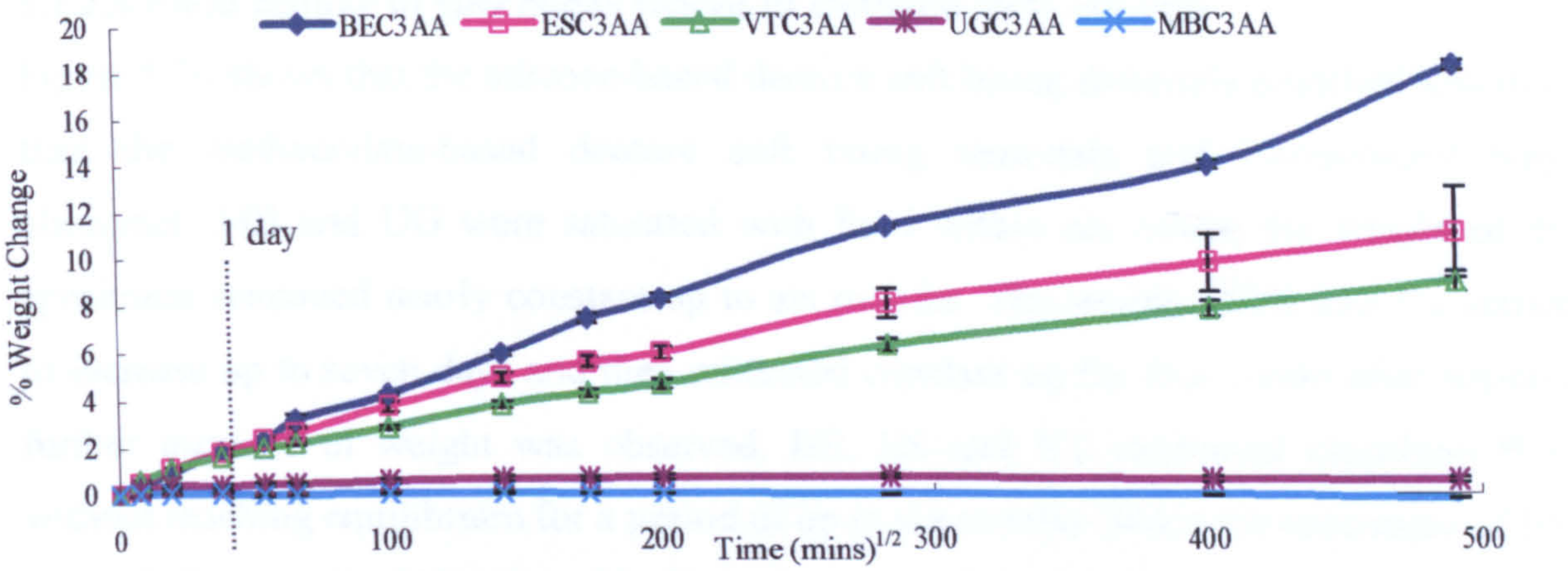


Figure 5.32 Mean percentage weight change of materials stored in changed 3% acetic acid.

Table 5.13 Summary of the fluid uptake of specimens after 6 months storage in 3% acetic acid (changed solution), mean (sd), (n=3)

Materials	% Weight change /C3AA	% Solubility /C3AA	% Real uptake /C3AA	Diffusion coefficient D_{abs} (10^{-13} m^2sec^{-1})
Vertex™Soft	8.95(0.51)	1.95(0.08)	10.91(0.46)	*
EverSoft®	11.05(1.95)	7.78(1.08)	18.83(3.02)	*
Molloplast-B®	-0.19(0.01)	0.56(0.04)	0.37(0.04)	4.24
Ufi Gel SC	0.58(0.10)	0.31(0.09)	0.89(0.15)	19.66
BE	18.19(0.20)	-0.36(0.08)	17.83(0.13)	*

* Diffusion coefficient for Vertex™Soft, EverSoft® and BE could not be determined since no equilibrium had been reached.

Table 5.13 and Fig 5.33 show that MB and UG absorbed less fluid than VT, ES and BE. The solubility of ES and VT was significantly higher than MB, UG, and BE ($p<0.05$). The ranking was ES > VT > MB > UG > BE. The real uptake of BE, ES and VT was significantly higher than MB and UG ($p<0.05$). The ranking was ES > BE > VT > UG > MB.

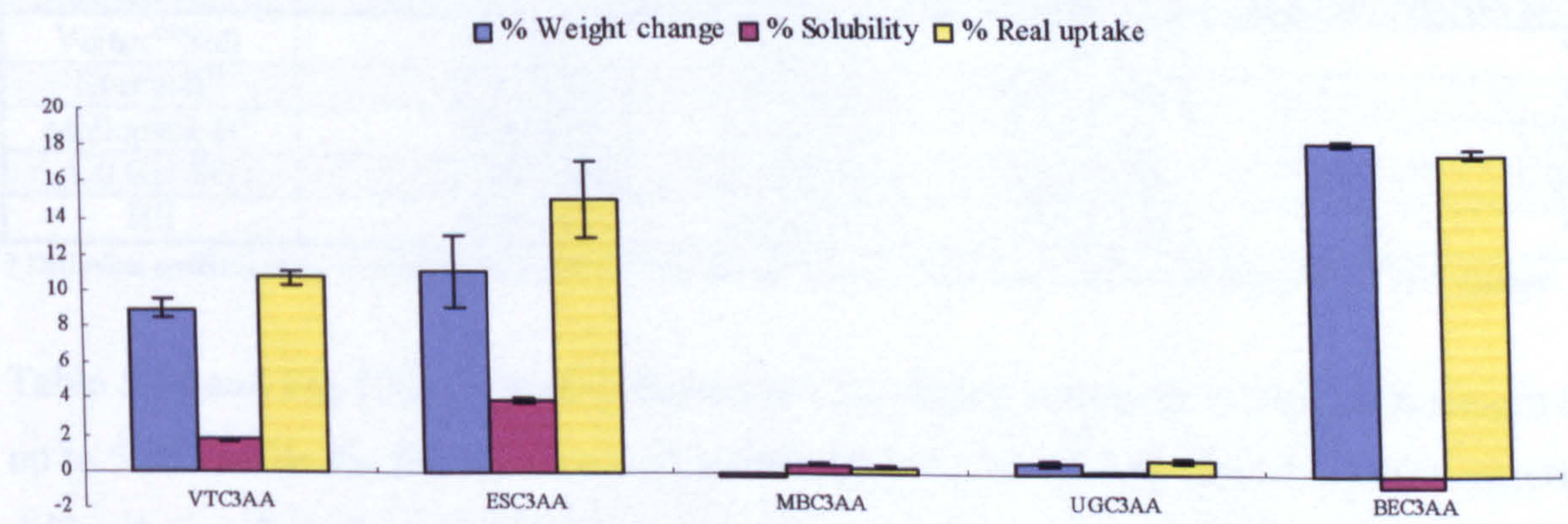


Figure 5.33 Bar chart of % weight change, solubility, and real uptake of materials in regularly changed 3% acetic acid at six months.

5.1.2.4 Fluid uptake of specimens stored in changed 10% ethanol

Figure 5.34 shows that the silicone-based denture soft lining materials absorbed less fluid than the methacrylate-based denture soft lining materials and bromo-butyl butyl elastomer. MB and UG were saturated with fluid within six hours; the weight of the specimens remained nearly constant up to six months. The weight of ES and VT started to increase up to seven days and then remained constant up for four weeks after which a further increase in weight was observed. BE, ES and VT continued absorbing fluid without reaching equilibrium for a period of up to six months. Since the specimens of ES, BE and VT stored in 10% ethanol had not reached equilibrium, the sorption parameters of these specimens could not be calculated.

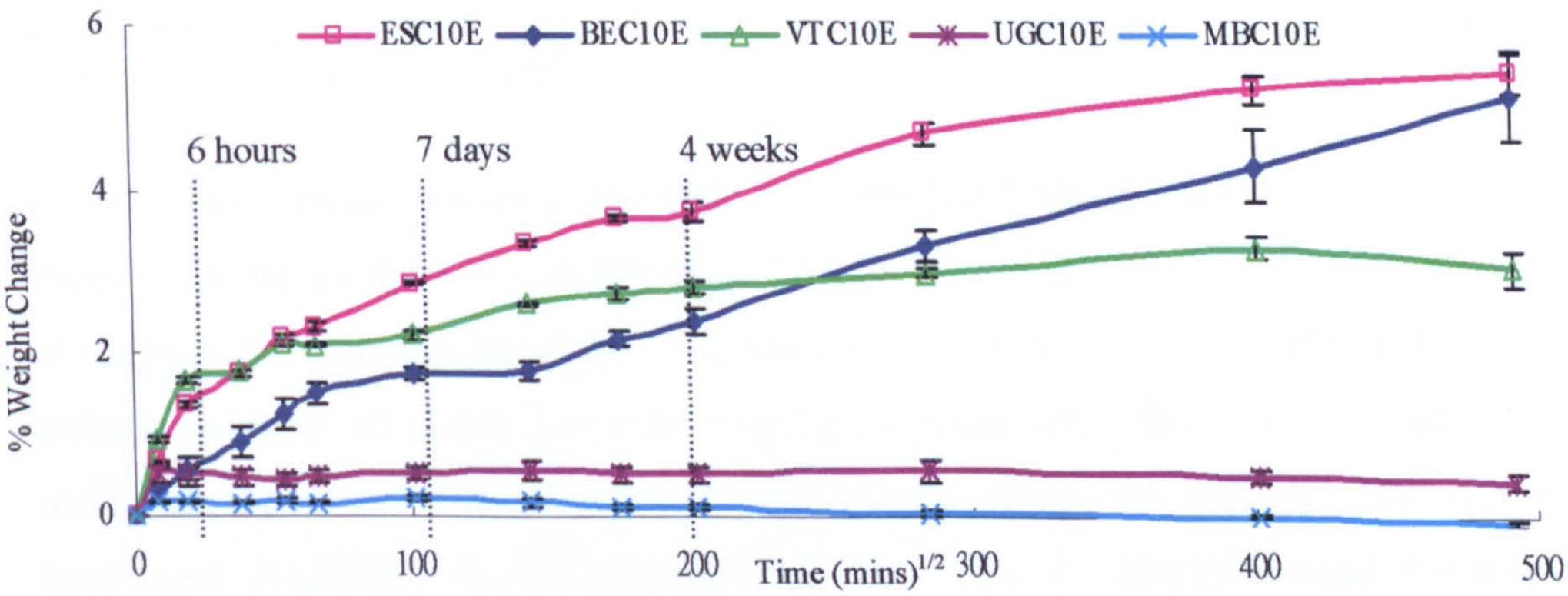


Figure 5.34 Mean percentage weight change of materials stored in changed 10% ethanol.

Table 5.14 Summary of the fluid uptake of specimens after 6 months storage in 10% ethanol (changed solution), mean (sd), (n=3).

Materials	% Weight change (C10E)	% Solubility (C10E)	% Real uptake (C10E)	Diffusion coefficient D_{abs} (10^{-13} m^2sec^{-1})
Vertex™Soft	3.03(0.21)	2.32(0.12)	5.35(0.27)	*
EverSoft®	5.39(0.28)	8.93(0.30)	14.32(0.10)	*
Molloplast-B®	-0.08(0.05)	0.52(0.10)	0.44(0.05)	3.79
Ufi Gel SC	0.44(0.08)	0.20(0.02)	0.63(0.09)	1.38
BE	5.09(0.55)	-0.46(0.01)	4.63(0.56)	*

* Diffusion coefficient for Vertex™Soft, EverSoft® and BE could not be determined since no equilibrium had been reached.

Table 5.14 and Fig 5.35 show that the denture soft lining materials increased in weight by up to 5.4% while the BE increased in weight up to 5.1%. The weight change for material differed significantly ($p<0.05$), the ranking being ES > BE > VT > UG > MB. The solubility of ES and VT was significantly higher than MB, UG, and BE ($p<0.05$), and the

ranking was ES > VT > MB > UG > BE. The real uptake of ES, BE and VT was significantly higher than MB and UG ($p<0.05$), and the ranking was ES > VT > BE > UG > MB.

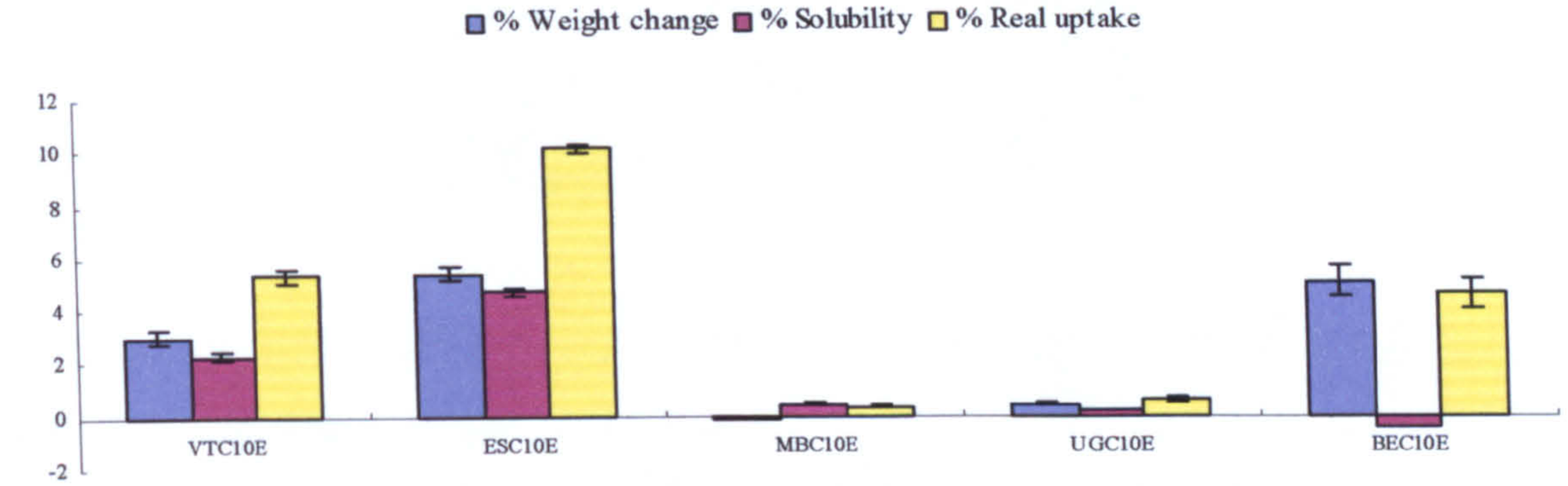


Figure 5.35 Bar chart of % weight change, solubility, and real uptake of materials in regularly changed 10% ethanol at six months.

5.1.2.5 Fluid uptake of specimens stored in changed 50% ethanol

Figure 5.36 shows that MB and UG were saturated with fluid within six hours; the weight of the specimens remained nearly constant up to six months. The weight of VT and ES quickly increase up to six hours and one day respectively, followed by a decrease in weight for eight weeks after which nearly constant weight was observed. BE showed a continuous increasing weight up to six months. The methacrylate-based denture soft lining materials and BE continued changing in weight without reaching equilibrium for a period of up to six months. Since the specimens of VT, ES and BE stored in 50% ethanol had not reached equilibrium, the sorption parameters of these specimens could not be calculated.

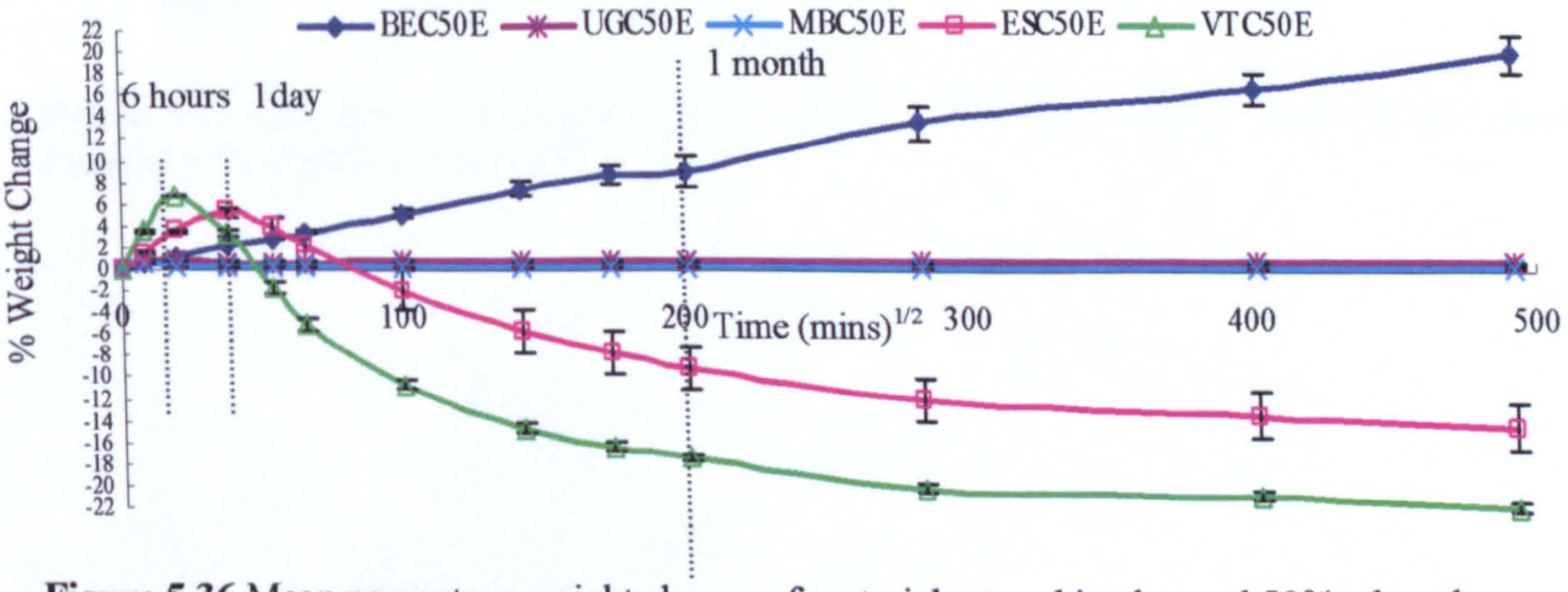


Figure 5.36 Mean percentage weight change of materials stored in changed 50% ethanol.

Table 5.15 Summary of the fluid uptake of specimens after 6 months storage in 50% ethanol (changed solution), mean (sd), (n=3)

Materials	% Weight change (C50E)	% Solubility (C50E)	% Real uptake (C50E)	Diffusion coefficient D_{abs} (10^{-13} m^2sec^{-1})
Vertex™Soft	-21.65(0.40)	33.02(0.16)	11.37(0.24)	*
EverSoft®	-14.31(2.07)	29.70(1.65)	15.39(0.47)	*
Molloplast-B®	0.24(0.02)	0.67(0.01)	0.91(0.01)	2.51
Ufi Gel SC	0.72(0.09)	0.23(0.03)	0.94(0.07)	8.36
BE	19.75(1.82)	0.31(0.03)	20.06(1.78)	*

* Diffusion coefficient for Vertex™Soft, EverSoft® and BE could not be determined since no equilibrium had been reached.

Table 5.15 and Fig 5.37 show the overall percentage weight change, solubility and real uptake in regularly changed 50% ethanol at six months. The greatest weight gain was observed with BE. No significant difference was observed in weight gain between MB and UG ($p>0.05$). A quite dramatic weight change for VT and ES in changed condition is exhibited. The greatest solubility was observed with VT and ES in changed 50% ethanol. Additionally, the real uptake of BE, ES and VT was significantly greater than MB and UG ($p<0.05$).

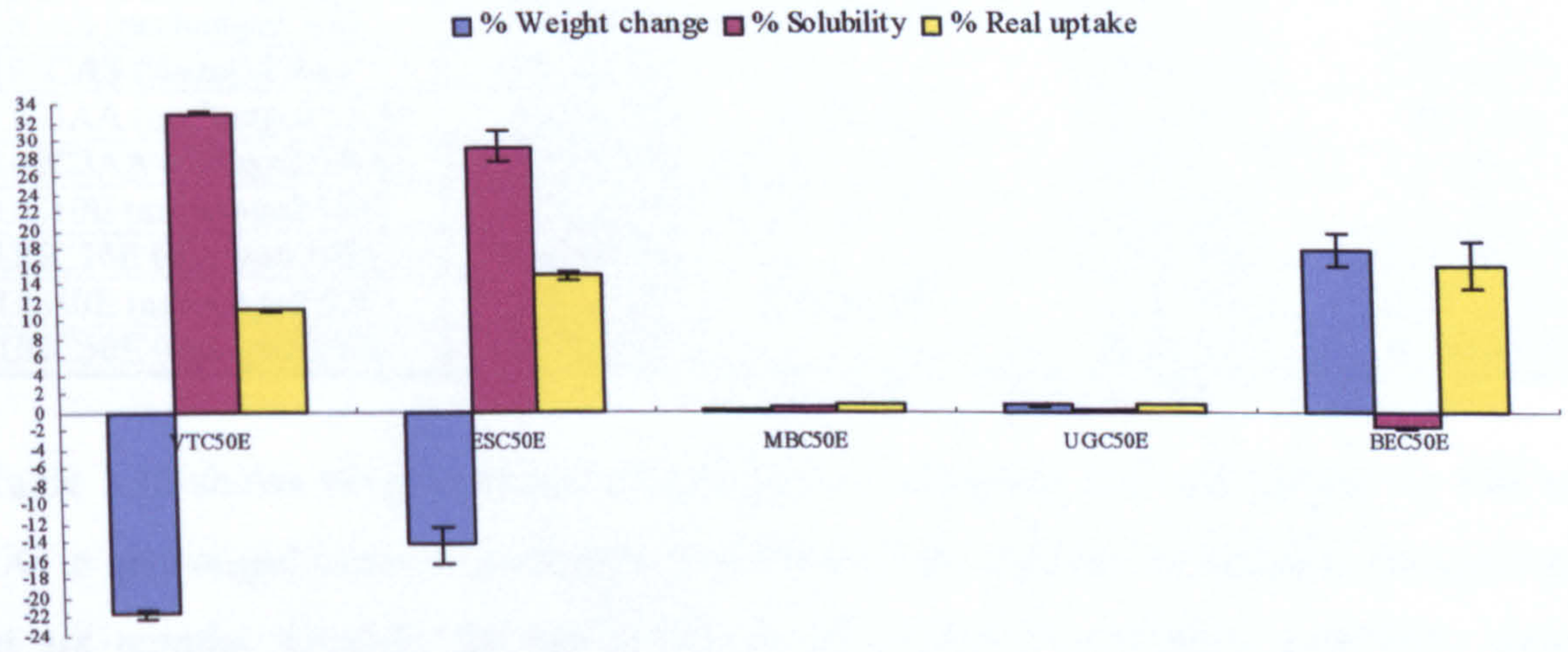


Figure 5.37 Bar chart of % weight change, solubility, and real uptake of materials in regularly changed 50% ethanol at six months.

5.1.3 Comparison between unchanged and changed storage media

5.1.3.1 Fluid uptake characterization of the silicone-based materials

Table 5.16 Summary of the fluid uptake characterisation of Molloplast-B® and Ufi Gel SC between unchanged at six months and one year and changed storage liquids at six months, mean (sd)

	% Weight change		% Solubility at one year for unchanged and at six months for changed	Real % uptake at one year for unchanged and at six months for changed
	Six months	One year		
MBDW (unchanged DW)	2.04 (0.10)	2.00 (0.11)	-1.36 (0.12)	0.64 (0.05)
MBCDW (changed DW)	-0.12 (0.02)		0.50 (0.10)	0.37 (0.08)
MBAS (unchanged AS)	2.58 (0.30)	2.31 (0.21)	-1.17 (0.15)	1.14 (0.14)
MBCAS (changed AS)	0.65 (0.11)		0.28 (0.16)	0.93 (0.07)
MB3AA (unchanged 3AA)	2.92 (0.17)	3.13 (0.16)	-2.00 (0.16)	1.13 (0.07)
MBC3AA (changed 3AA)	-0.19 (0.01)		0.56 (0.04)	0.37 (0.04)
MB10E (unchanged 10E)	2.65 (0.05)	2.62 (0.03)	-1.73 (0.06)	0.89 (0.04)
MBC10E (changed 10E)	-0.08 (0.05)		0.52 (0.10)	0.44 (0.05)
MB50E (unchanged 50E)	2.48 (0.10)	2.68 (0.14)	-1.47 (0.15)	1.21 (0.05)
MBC50E (changed 50E)	0.24 (0.02)		0.67 (0.01)	0.91 (0.01)
UGDW (unchanged DW)	2.00 (0.22)	1.92 (0.24)	-1.43 (0.24)	0.50 (0.04)
UGCDW (changed DW)	0.19 (0.08)		0.29 (0.09)	0.48 (0.11)
UGAS (unchanged AS)	1.70 (0.16)	1.48 (0.15)	-0.80 (0.13)	0.68 (0.03)
UGCAS (changed AS)	0.26 (0.06)		0.45 (0.04)	0.71 (0.07)
UG3AA (unchanged 3AA)	1.82 (0.17)	1.80 (0.18)	-0.92 (0.18)	0.88 (0.08)
UGC3AA (changed 3AA)	0.58 (0.10)		0.31 (0.09)	0.89 (0.15)
UG10E (unchanged 10E)	1.36 (0.23)	1.37 (0.23)	-0.86 (0.26)	0.51 (0.03)
UGC10E (changed 10E)	0.44 (0.08)		0.20 (0.02)	0.63 (0.09)
UG50E (unchanged 50E)	1.91 (0.07)	1.94 (0.08)	-1.32 (0.09)	0.62 (0.08)
UGC50E (changed 50E)	0.72 (0.09)		0.23 (0.03)	0.94 (0.07)

Table 5.16 shows the percentage weight change, solubility and real uptake for MB and UG in unchanged storage liquid at six months and one year and in changed storage liquid at six months. Overall, the specimens in all conditions exhibited very little weight change, very slight solubility and small real uptake.

5.1.3.2 Fluid uptake characterization of the methacrylate-based materials

Table 5.17 Summary of the fluid uptake characterisation of Vertex™Soft and EverSoft® between unchanged at six months and one year and changed storage liquids at six months, mean (sd)

	% Weight change		% Solubility at one year for unchanged and at six months for changed	Real % uptake at one year for unchanged and at six months for changed
	Six months	One year		
VTDW (unchanged DW)	2.71 (0.30)	3.08 (0.39)	1.26 (0.12)	4.34 (0.39)
VTCDW (changed DW)	2.14 (0.54)		1.27 (0.10)	3.41 (0.54)
VTAS (unchanged AS)	1.01 (0.69)	-2.94 (1.26)	7.93 (1.11)	4.99 (0.40)
VTCAS (changed AS)	1.22 (0.70)		6.57 (0.39)	7.79 (0.09)
VT3AA (unchanged 3AA)	10.03 (1.07)	13.10 (1.21)	1.51 (0.10)	14.61 (1.19)
VTC3AA (changed 3AA)	8.95 (0.51)		1.95 (0.08)	10.91 (0.46)
VT10E (unchanged 10E)	2.97 (0.15)	3.22 (0.22)	0.94 (0.24)	4.16 (0.13)
VTC10E (changed 10E)	3.03 (0.21)		2.32 (0.12)	5.35 (0.27)
VT50E (unchanged 50E)	2.49 (1.29)	4.58 (1.90)	6.33 (3.23)	10.90 (2.11)
VTC50E (changed 50E)	-21.65 (0.40)		33.02 (0.16)	11.37 (0.24)
ESDW (unchanged DW)	3.88 (0.32)	4.83 (0.34)	13.45 (0.44)	18.28 (0.68)
ESCDW (changed DW)	6.75 (0.56)		8.41 (1.06)	15.16 (1.62)
ESAS (unchanged AS)	-2.73 (0.64)	-5.90 (0.63)	16.38 (0.45)	10.48 (0.47)
ESCAS (changed AS)	4.09 (0.66)		9.30 (0.83)	13.38 (1.17)
ES3AA (unchanged 3AA)	14.40 (0.88)	19.23 (1.39)	11.26 (0.75)	30.48 (1.84)
ESC3AA (changed 3AA)	11.05 (1.95)		7.78 (1.08)	18.83 (3.02)
ES10E (unchanged 10E)	5.71 (0.29)	6.95 (0.52)	13.48 (0.36)	20.43 (0.69)
ESC10E (changed 10E)	5.39 (0.28)		8.93 (0.30)	14.32 (0.10)
ES50E (unchanged 50E)	1.26 (2.67)	6.79 (2.64)	12.41 (0.81)	19.20 (2.37)
ESC50E (changed 50E)	-14.31 (2.07)		29.70 (1.65)	15.39 (0.47)

Table 5.17 shows the percentage weight change, solubility and real uptake for VT and ES in unchanged storage liquid at six months and one year and in changed storage liquid at six months. The specimens in unchanged 3% acetic acid showed the highest weight increase (13.1% and 19.2%) and in changed 50% ethanol exhibited the greatest loss of weight (21.7% and 14.3%). The specimens in changed 50% ethanol exhibited the highest solubility (33.0% and 29.7%) even though this was after only six months. The percentage real uptake in unchanged and changed solution differed significantly ($p<0.05$), but account must also be taken of the different immersion time periods.

5.1.3.3 Fluid uptake characterization of bromo-butyl butyl elastomer

Table 5.18 Summary of the fluid uptake characterisation of bromo-butyl butyl elastomer between unchanged at six months and one year and changed storage liquids at six months, mean (sd)

	% Weight change		% Solubility at one year for unchanged and at six months for changed	Real % uptake at one year for unchanged and at six months for changed
	Six months	One year		
BEDW (unchanged DW)	6.40 (1.06)	9.71 (1.86)	-0.29 (0.13)	9.42 (1.86)
BECDW (changed DW)	6.47 (0.85)		-0.70 (0.09)	5.77 (0.79)
BEAS (unchanged AS)	5.41 (0.87)	7.13 (1.32)	0.39 (0.40)	7.52 (1.02)
BECAS (changed AS)	14.55 (2.26)		-0.68 (0.11)	13.87 (2.35)
BE3AA (unchanged 3AA)	18.50 (1.91)	26.00 (1.21)	-0.25 (0.46)	25.75 (1.10)
BEC3AA (changed 3AA)	18.19 (0.20)		-0.36 (0.08)	17.83 (0.13)
BE10E (unchanged 10E)	6.49 (0.53)	12.48 (1.14)	-0.30 (0.17)	12.19 (1.07)
BEC10E (changed 10E)	5.09 (0.55)		-0.46 (0.01)	4.63 (0.56)
BE50E (unchanged 50E)	12.90 (1.17)	16.30 (1.11)	-0.67 (0.09)	15.63 (1.11)
BEC50E (changed 50E)	19.75 (1.82)		0.31 (0.03)	20.06 (1.78)

Table 5.18 shows the percentage weight change, solubility and real uptake for BE in unchanged at six months and one year and changed storage liquids at six months. The specimens in unchanged 3% acetic acid showed the highest weight increase at one year (26.0%). At six months the specimens in changed 50% ethanol exhibited the highest weight increase (19.8%). The percentage real uptake in unchanged and changed solution differed significantly ($p<0.05$), but account must also be taken of the different immersion time periods.

5.1.4 Visual assessment

Examples of the dimensional changes and surface quality of soft lining materials immersed in food simulating liquids are illustrated in Figs 5.38-42. These changes varied depending on the food simulating liquids in which the materials were immersed and the different generic types of denture soft lining material and elastomer.

The dimensional changes of BE after immersion in food simulating liquids at one month are shown in Figure 5.38. There is obviously swelling after immersion in CO and HB, but no obvious change in DW, AS, 3AA, 10E and 50E. Samples immersed in HB had disintegrated at four months.

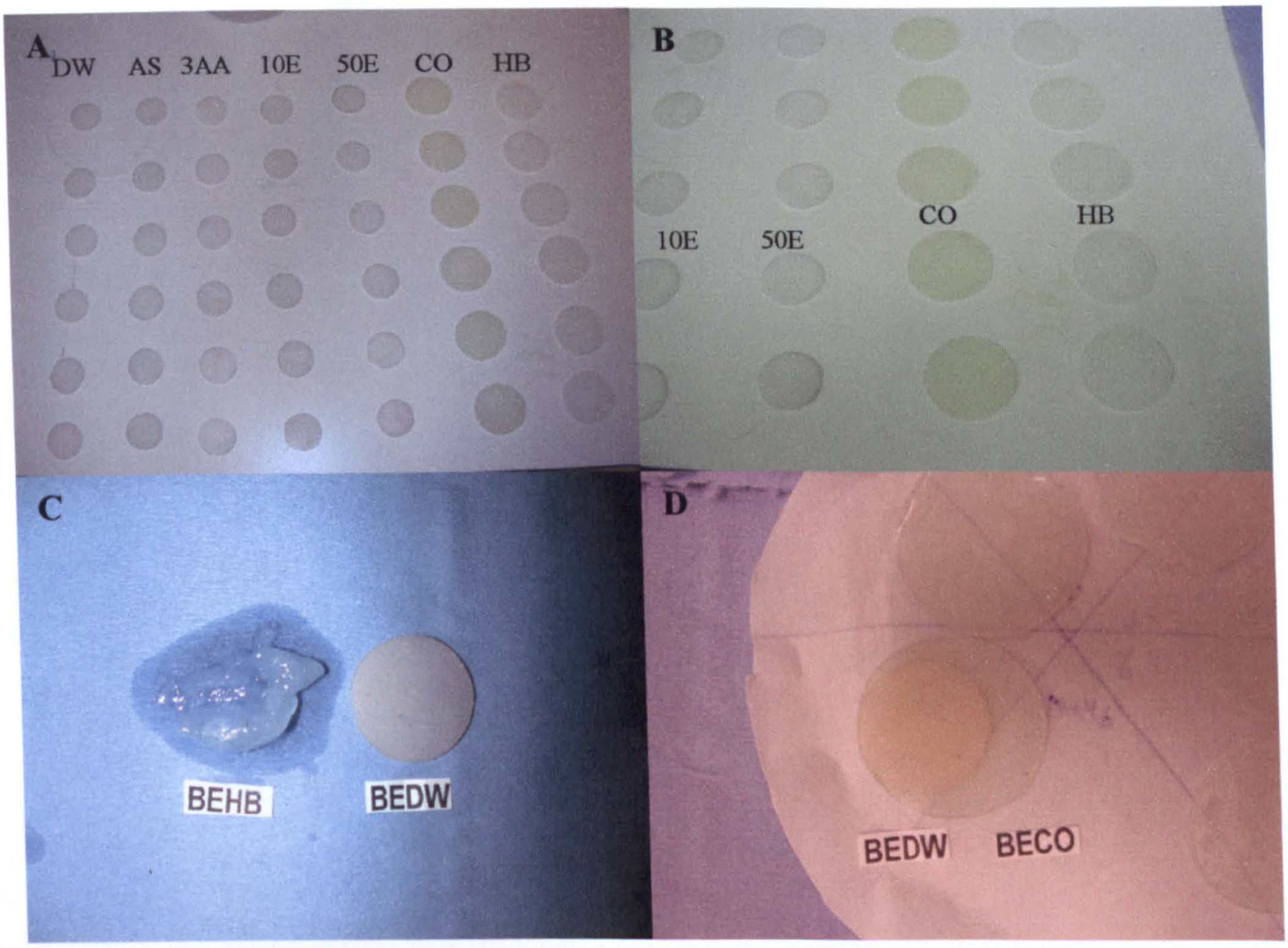


Figure 5.38 Samples of bromo-butyl butyl elastomer. **A**, Samples immersed in food simulating liquids at one month (from left to right: DW, AS, 3AA, 10E, 50E, CO and HB); **B**, Samples immersed in 10E, 50E, CO and HB (from left to right) at one month; **C**, Samples immersed HB compared with a sample immersed in DW at four months; **D**, Samples immersed in CO compared with a sample immersed in DW at four months.

Examples of the dimensional changes of samples of VT and MB at one year are shown in Figure 5.39. There were no obviously changes in DW, 3AA, 10E and 50E. However, there was slight shrinkage of VT compared with MB in AS, 50E, CO and HB.

The dimensional changes of samples of ES compared with samples of MB at one year are shown in Figure 5.40. All samples of ES showed a moderate shrinkage compared with MB after immersion in food simulating liquids at one year.

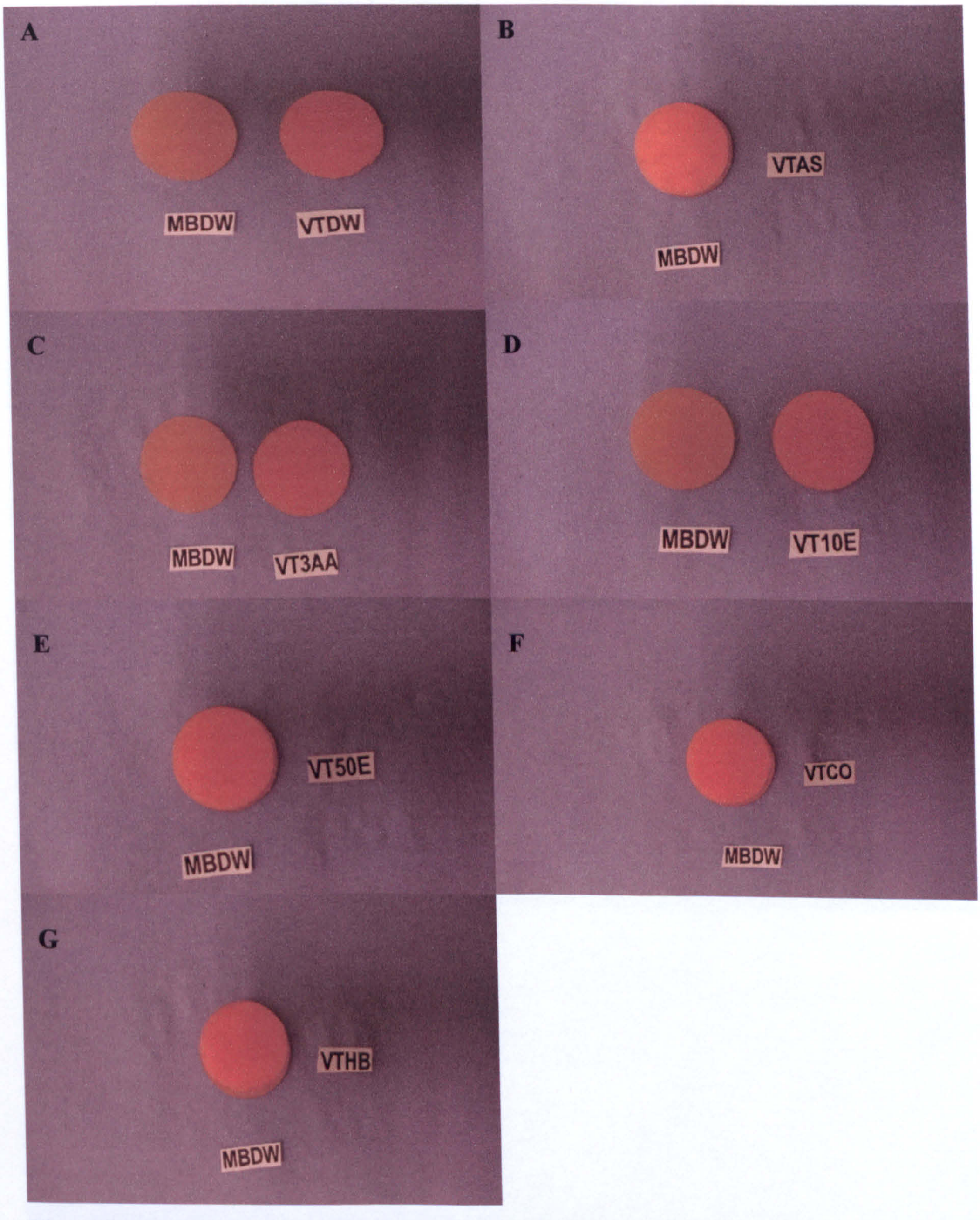


Figure 5.39 Dimensional changes of samples of VT immersed in food simulating liquids in each case compared to a sample of MB at one year. **A**, Samples immersed in DW; **B**, Sample immersed in AS; **C**, Sample immersed in 3AA; **D**, Sample immersed in 10E; **E**, Sample immersed in 50E; **F**, Sample immersed in CO; **G**, Sample immersed in HB. VTAS, VT50E, VTCO and VTHB samples are on top of the MBDW samples demonstrating the slight shrinkage of the former.

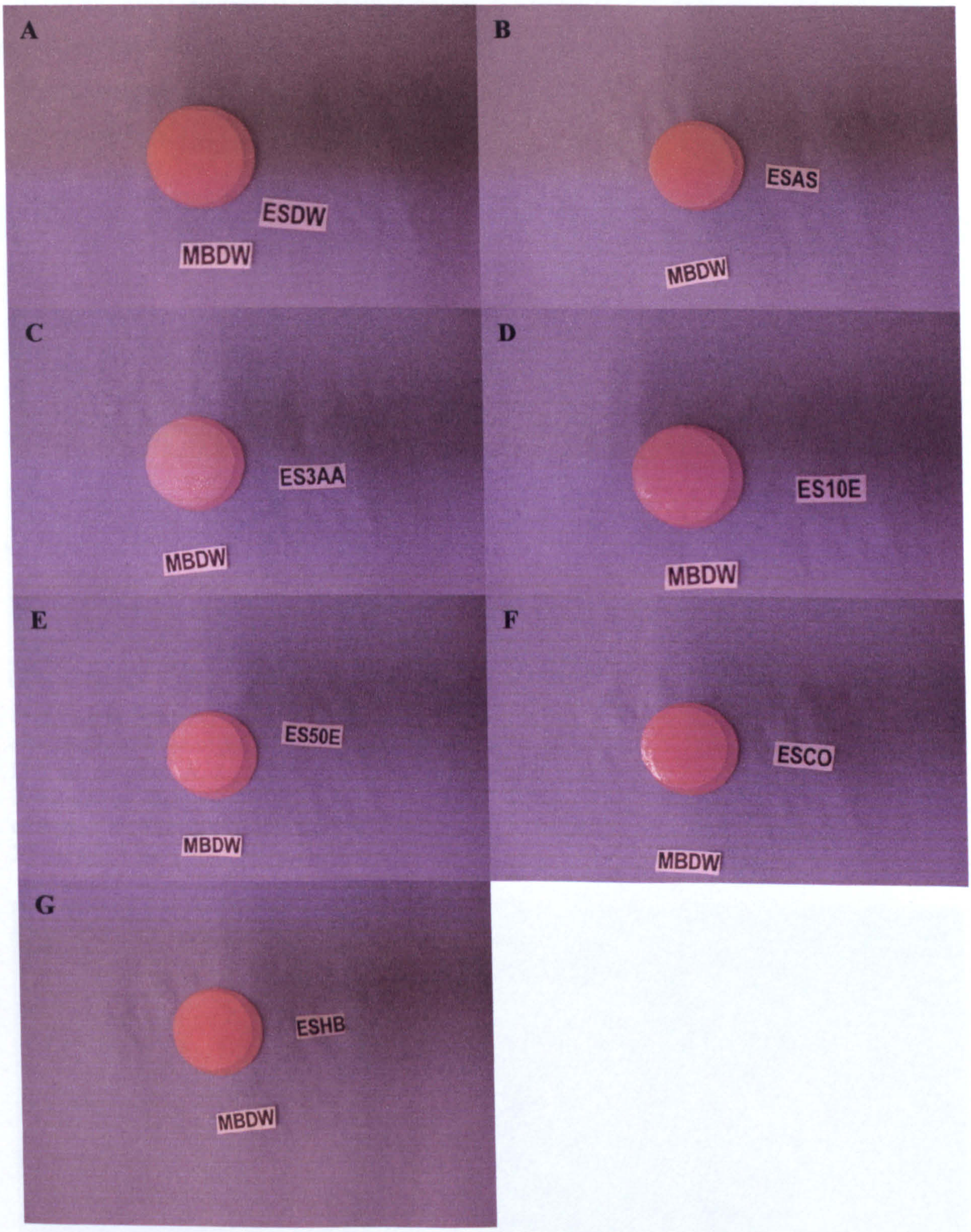


Figure 5.40 Dimensional changes of samples of ES immersed in food simulating liquids in each case compared a sample of MB at one year. **A**, Samples immersed in DW; **B**, Samples immersed in AS; **C**, Samples immersed in 3AA; **D**, Samples immersed in 10E; **E**, Samples immersed in 50E; **F**, Samples immersed in CO; **G**, Samples immersed in HB. The ES sample is always on top of the MBDW sample.

The dimensional changes of samples of VT and ES compared with MB in changed 50E at six months and unchanged 50E at one year are shown in Figure 5.41. Samples in changed 50E showed much more dimensional change than in unchanged immersing fluids. Figure 5.42 shows minor voids on the ES after immersion in 3AA at one month.

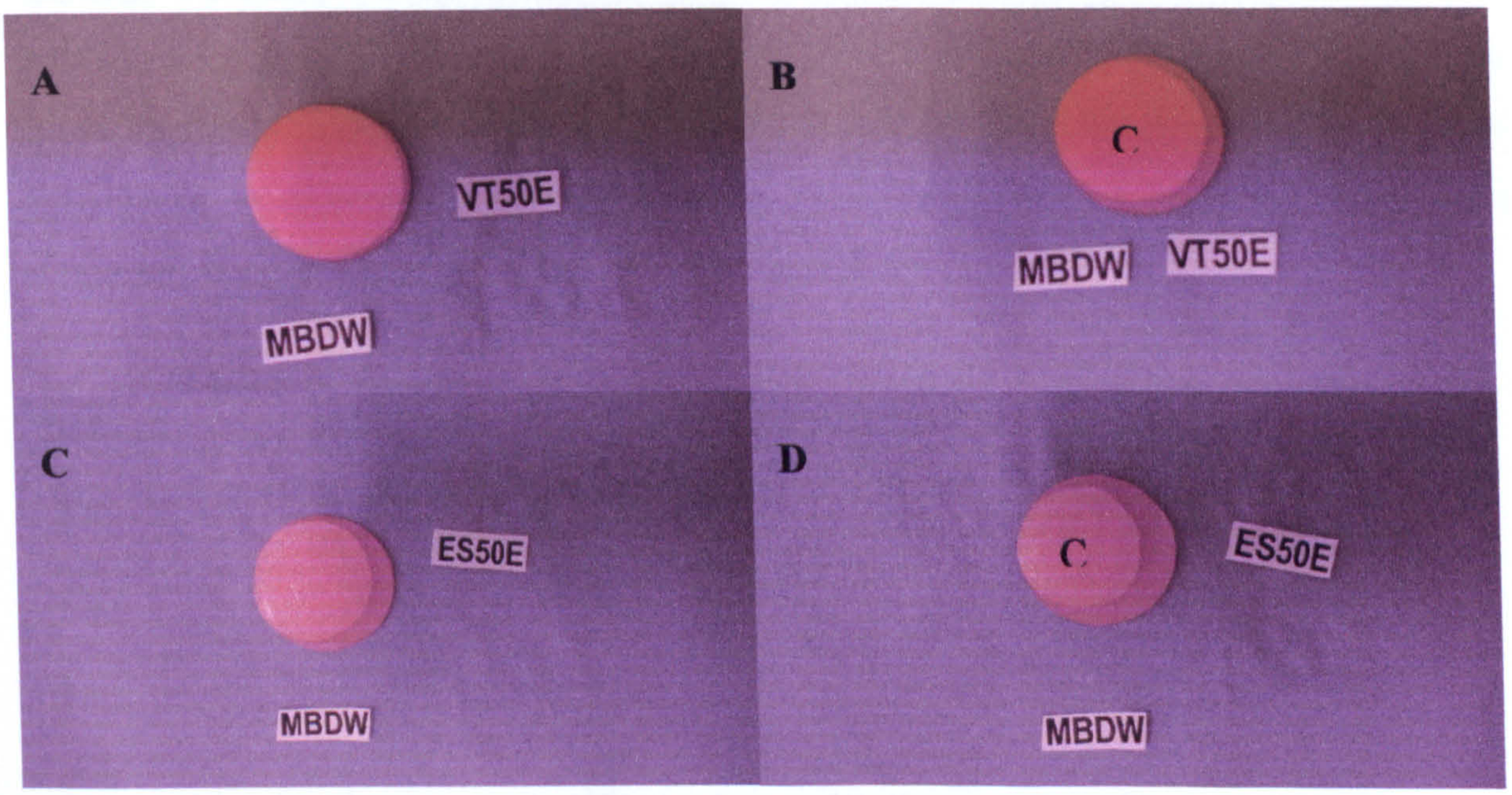


Figure 5.41 Samples of VT and ES compared with MB following immersion in unchanged 50E at one year and in changed 50E at six months in each case compared a sample of MB immersed in DW at one year. **A**, Sample of VT immersed in unchanged 50E at one year; **B**, Samples of VT immersed in changed (C) 50E at six months; **C**, Samples of ES immersed in unchanged 50E at one year; **D**, Samples of ES immersed in changed (C) 50E at six months. In each case the VT or ES sample is on top of the MBDW sample.

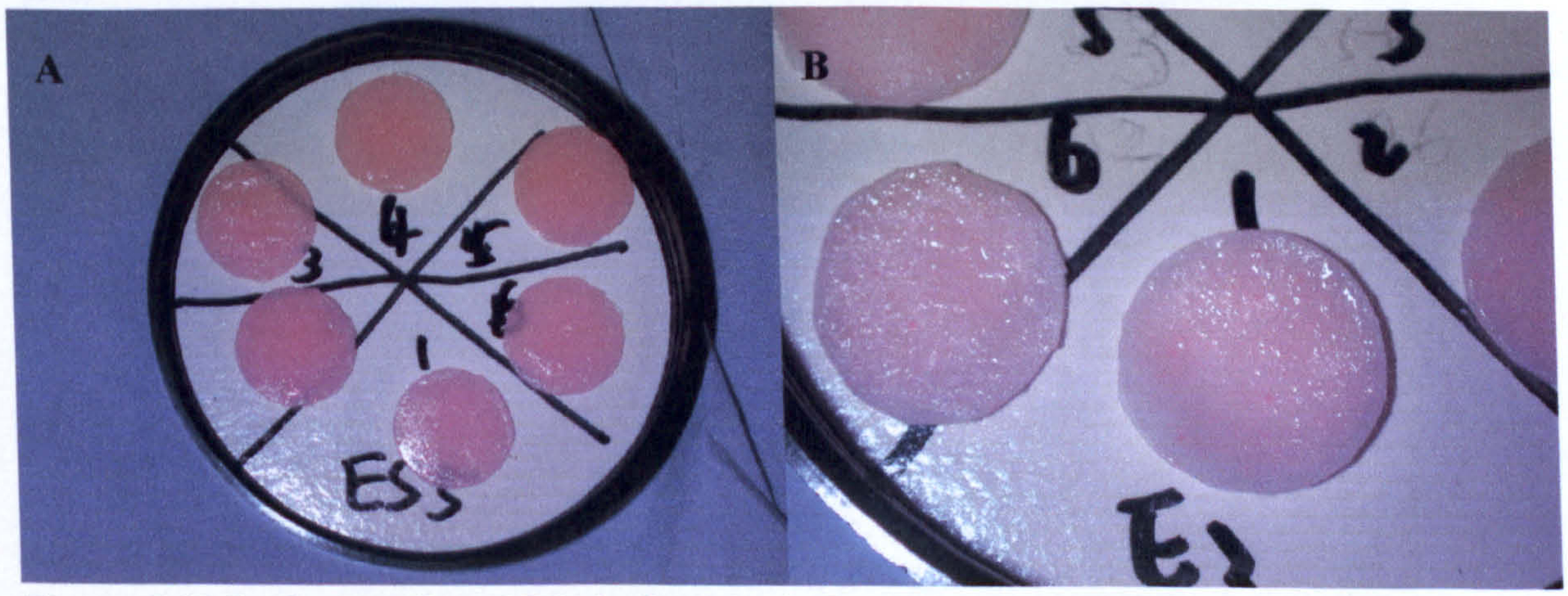


Figure 5.42 Surface quality of ES. **A**, Samples before immersion; **B**, Samples immersed in 3AA at one month.

The results of visual assessment are shown in Tables 5.19-20. These dimensional changes varied depending on immersion fluids and types of the denture soft lining materials and elastomer. Dimensional changes were observed with combinations of VT-AS, VT-50E, VT-CO, VT-HB, ES-DW, ES-AS, ES-3AA, ES-10E, ES-50E, ES-CO, ES-HB, BE-CO, BE-HB, VT-CAS, VT-C50E, ES-CDW, ES-CAS, ES-C3AA, ES-C10E and ES-C50E. More severe changes (swelling) were observed with samples of BE immersed in oils than those immersed in other liquids (Figure 5.38 and Table 5.19). More dimensional changes (shrinkage) were observed with samples of ES immersed in changed 50E than those immersed in other liquids (Figure 5.41 and Table 5.20).

Table 5.19 Grade of dimensional change of denture soft lining materials immersed in unchanged food simulating liquids for one year (* Grade observed at two months).

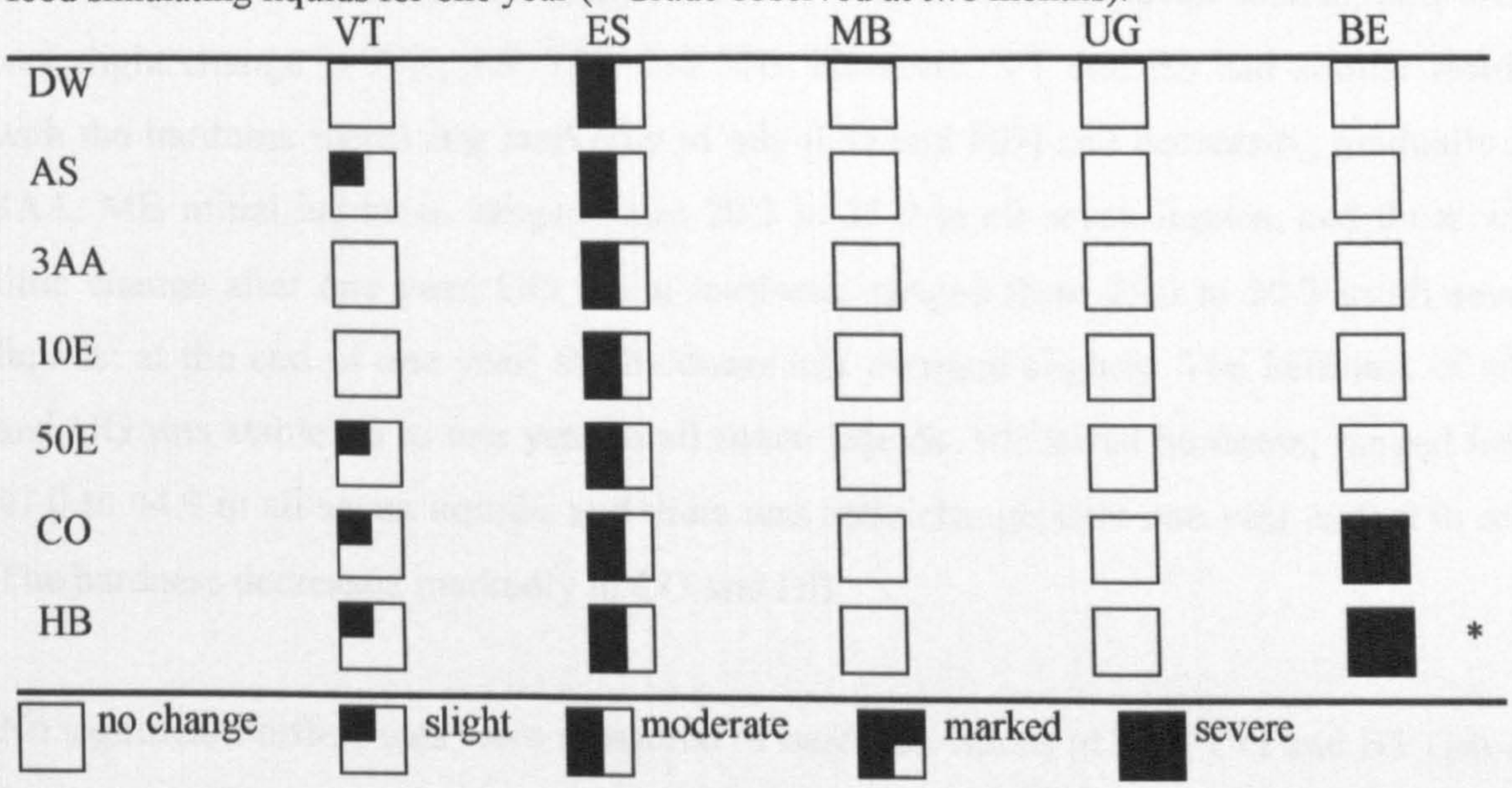
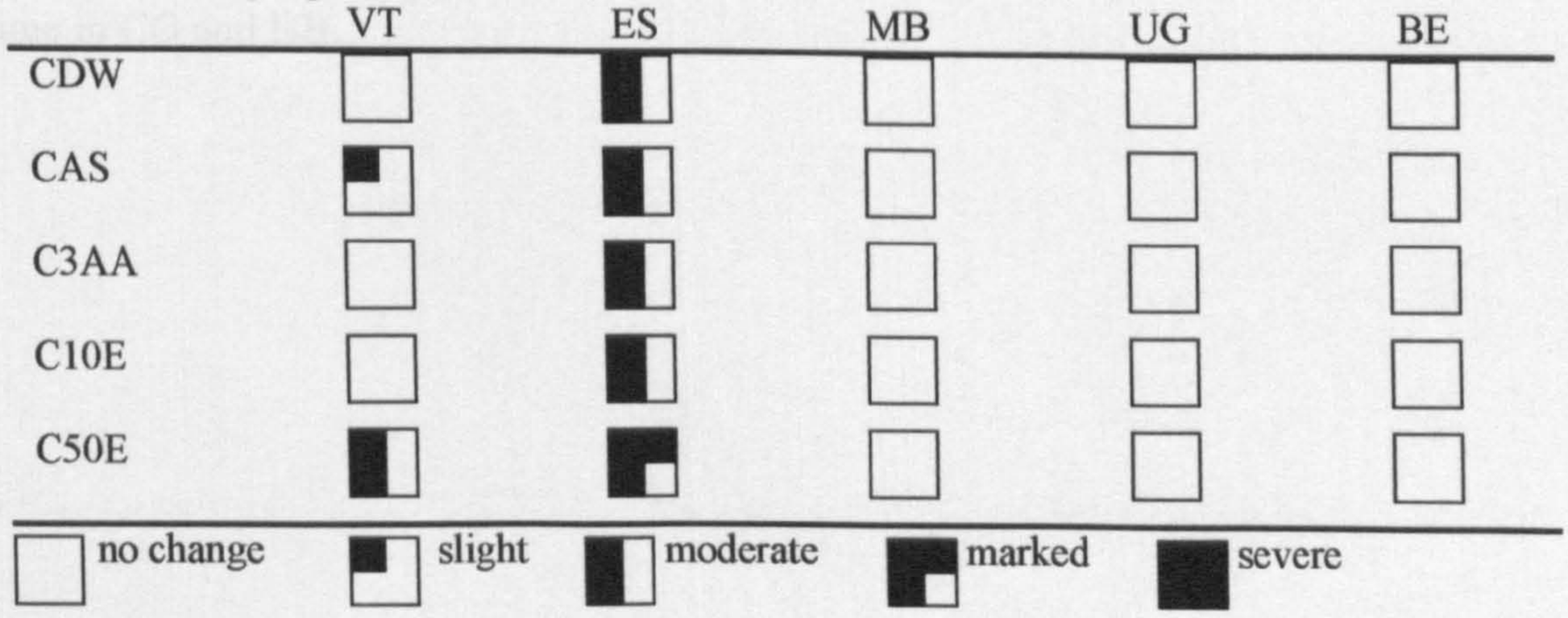


Table 5.20 Grade of dimensional change of denture soft lining materials immersed in changed food simulating liquids for six months.



5.2 Shore A Hardness Evaluation

5.2.1 Specimens stored in food simulating liquids

The hardness values of five materials stored in seven food simulating liquids, measured with a Shore A durometer, are listed (see Tables 5.21-27). The hardness of the denture soft lining materials as determined by the Shore A durometer readings, ranged from 13.0 to 87.4. This value is an indication of the liner compliance. The smaller the number, the greater the compliance. VT initial hardness, ranged from 47.5 to 53.9 in all seven liquids, and there was little change in DW, AS, 10E and 50E. However, the hardness increased markedly in CO and HB and decreased gradually in 3AA. ES was fairly soft after processing, its initial hardness, ranged from 25.6 to 33.0 in all seven liquids, and there was slight change in DW, AS, 10E and 50E. However, VT and ES had similar results with the hardness increasing markedly in oils (CO and HB) and decreasing gradually in 3AA. MB initial hardness, ranged from 29.3 to 35.9 in all seven liquids, and there was little change after one year. UG initial hardness, ranged from 23.0 to 30.3 in all seven liquids: at the end of one year, the hardness had changed slightly. The hardness of MB and UG was stable up to one year in all seven liquids. BE initial hardness, ranged from 41.0 to 44.9 in all seven liquids, and there was little change after one year except in oils. The hardness decreased markedly in CO and HB.

No significant differences were measured in hardness values of MB, UG and BE (except in oils) at different time intervals. However, VT and ES were found to be significantly harder with time in CO and HB. Conversely, BE was found to be significantly softer with time in CO and HB.

Table 5.21 Shore A hardness for specimens stored in distilled water at 37±1°C, mean (sd)

Test period	Liquid (distilled water)				
	Vertex™Soft	EverSoft®	Molloplast-B®	Ufi Gel SC	BE
Initial	53.7 (2.2)	31.0 (1.9)	31.6 (2.1)	31.3 (3.4)	41.0 (1.8)
0.5 hour	49.3 (2.0)	30.7 (1.0)	31.3 (1.4)	31.1 (2.2)	44.3 (2.9)
1 hour	50.3 (1.4)	29.3 (1.4)	30.2 (1.1)	30.0 (2.6)	44.4 (2.3)
2 hours	50.0 (1.4)	29.0 (1.5)	29.8 (1.4)	29.3 (3.3)	44.3 (2.3)
4 hours	51.3 (1.2)	29.5 (1.7)	30.3 (1.2)	29.5 (3.1)	43.1 (2.7)
6 hours	49.8 (1.5)	29.3 (0.9)	29.7 (1.0)	29.3 (2.1)	42.5 (3.1)
1 day	50.0 (1.3)	31.0 (1.5)	31.3 (1.3)	30.3 (2.4)	43.6 (2.6)
2 days	53.4 (1.3)	32.1 (1.6)	32.8 (1.5)	31.8 (2.7)	43.6 (2.8)
3 days	51.5 (1.1)	32.3 (1.3)	32.6 (1.1)	31.8 (2.4)	43.3 (2.5)
1 week	53.3 (1.2)	33.0 (1.6)	33.4 (1.6)	32.1 (2.7)	42.8 (3.2)
2 weeks	49.3 (2.2)	31.1 (1.4)	31.8 (1.5)	30.7 (2.7)	42.5 (2.5)
3 weeks	47.5 (1.4)	29.7 (1.4)	30.2 (1.6)	29.3 (3.6)	39.3 (2.9)
1 month	46.9 (1.2)	28.9 (1.4)	29.5 (1.6)	28.7 (1.9)	40.8 (2.6)
2 months	45.7 (1.5)	26.9 (1.4)	27.7 (1.9)	27.0 (2.2)	40.0 (2.9)
4 months	46.6 (1.5)	26.1 (1.2)	27.0 (1.7)	26.7 (1.8)	43.0 (2.3)
6 months	45.7 (1.4)	26.6 (0.9)	27.7 (1.6)	27.7 (2.8)	41.1 (1.7)
1 year	47.2 (2.6)	24.2 (1.8)	25.7 (2.3)	26.4 (2.7)	42.7 (2.2)

Table 5.22 Shore A hardness for specimens stored in artificial saliva at 37±1°C, mean (sd)

Test period	Liquid (artificial saliva)				
	Vertex™Soft	EverSoft®	Molloplast-B®	Ufi Gel SC	BE
Initial	49.1 (2.4)	28.7 (3.1)	28.2 (2.0)	27.7 (1.5)	42.8 (1.9)
0.5 hour	49.5 (2.6)	29.3 (3.1)	28.9 (1.8)	28.5 (1.9)	41.6 (1.9)
1 hour	50.0 (2.1)	30.0 (3.0)	29.2 (1.8)	28.7 (2.1)	42.8 (2.0)
2 hours	48.5 (2.5)	29.3 (2.7)	28.7 (2.0)	28.0 (2.2)	42.5 (1.8)
4 hours	48.2 (2.4)	29.0 (2.8)	28.5 (1.3)	28.5 (2.5)	44.4 (1.8)
6 hours	49.8 (2.3)	29.8 (3.1)	28.9 (1.7)	28.5 (2.1)	42.3 (2.0)
1 day	51.1 (2.3)	30.5 (3.5)	29.3 (2.0)	28.5 (2.6)	43.4 (2.0)
2 days	51.0 (2.5)	31.5 (2.7)	30.5 (1.5)	29.8 (2.1)	44.3 (2.2)
3 days	51.3 (2.8)	31.8 (2.9)	30.3 (2.1)	29.2 (2.7)	43.0 (1.9)
1 week	47.0 (2.6)	29.7 (3.2)	28.4 (1.9)	26.9 (3.1)	43.3 (1.9)
2 weeks	48.4 (2.6)	30.3 (3.2)	28.5 (2.0)	27.5 (2.6)	42.3 (2.7)
3 weeks	45.9 (2.6)	29.3 (3.0)	27.7 (2.0)	27.0 (2.5)	40.8 (2.0)
1 month	44.1 (2.6)	27.2 (3.0)	25.9 (2.0)	25.2 (1.5)	41.6 (1.7)
2 months	44.3 (2.5)	28.0 (2.9)	26.7 (1.9)	26.1 (2.1)	41.1 (2.0)
4 months	43.9 (2.4)	27.0 (3.0)	26.1 (2.0)	25.4 (1.4)	44.8 (1.5)
6 months	46.2 (2.5)	29.3 (2.7)	28.5 (1.8)	27.5 (1.6)	44.1 (1.8)
1 year	53.9 (4.3)	32.5 (3.0)	31.3 (1.4)	30.3 (2.5)	44.8 (1.8)

Table 5.23 Shore A hardness for specimens stored in 3% acetic acid at 37±1°C, mean (sd)

Test period	Liquid (3% acetic acid)				
	Vertex™Soft	**EverSoft®**	**Molloplast-B®**	**Ufi Gel SC**	**BE**
Initial	53.1 (3.1)	29.3 (2.5)	35.9 (0.9)	27.7 (2.3)	42.5 (2.0)
0.5 hour	52.0 (2.7)	27.8 (2.4)	34.6 (0.7)	25.9 (2.4)	41.1 (2.0)
1 hour	48.2 (3.7)	26.1 (2.3)	33.9 (0.8)	26.9 (3.2)	41.3 (2.2)
2 hours	47.5 (2.4)	26.1 (2.6)	33.3 (0.7)	26.6 (2.9)	41.0 (2.0)
4 hours	50.7 (3.2)	27.7 (2.8)	33.4 (0.9)	26.0 (2.9)	43.3 (2.2)
6 hours	48.2 (2.8)	26.9 (2.3)	32.8 (0.8)	26.3 (1.6)	42.1 (2.0)
1 day	49.5 (3.2)	27.5 (2.6)	33.4 (0.7)	27.4 (2.7)	42.3 (2.4)
2 days	50.3 (3.2)	27.7 (2.6)	33.6 (0.9)	28.2 (2.4)	43.6 (2.3)
3 days	45.9 (2.7)	26.1 (2.3)	33.8 (1.1)	27.7 (2.8)	41.3 (1.9)
1 week	50.5 (2.0)	27.9 (2.7)	33.6 (0.9)	25.2 (2.1)	41.6 (1.8)
2 weeks	49.8 (2.7)	25.6 (2.8)	33.3 (0.9)	26.3 (2.4)	40.2 (2.1)
3 weeks	49.2 (3.5)	24.8 (2.4)	32.8 (1.2)	25.4 (2.4)	38.5 (1.6)
1 month	40.7 (2.7)	22.0 (2.5)	32.6 (1.2)	29.0 (2.4)	38.7 (2.2)
2 months	43.3 (3.2)	21.0 (2.4)	32.5 (1.0)	27.7 (3.1)	37.2 (1.8)
4 months	40.8 (2.5)	17.7 (2.7)	32.1 (0.8)	29.7 (3.6)	37.7 (2.2)
6 months	41.0 (2.9)	19.7 (2.8)	31.8 (0.5)	30.5 (2.0)	37.0 (2.0)
1 year	405 (2.6)	13.0 (2.8)	32.5 (0.7)	29.0 (4.0)	36.9 (2.3)

Table 5.24 Shore A hardness for specimens stored in 10% ethanol at 37±1°C, mean (sd)

Test period	Liquid (10% ethanol)				
	Vertex™Soft	**EverSoft®**	**Molloplast-B®**	**Ufi Gel SC**	**BE**
Initial	48.9 (2.0)	29.3 (2.0)	29.3 (0.9)	30.3 (1.7)	43.6 (1.7)
0.5 hour	53.9 (2.8)	30.0 (2.0)	30.0 (0.6)	30.0 (1.8)	43.0 (1.4)
1 hour	52.5 (2.4)	29.0 (1.7)	29.5 (0.8)	30.4 (1.6)	43.8 (1.2)
2 hours	50.8 (2.7)	28.0 (1.9)	28.5 (0.8)	29.8 (2.0)	43.1 (1.2)
4 hours	48.4 (2.0)	28.5 (1.4)	29.2 (1.0)	30.2 (1.6)	44.9 (1.3)
6 hours	48.7 (2.2)	28.2 (1.6)	29.0 (1.3)	30.0 (1.7)	43.4 (1.5)
1 day	48.4 (2.0)	28.5 (1.5)	29.3 (1.4)	30.2 (2.2)	44.9 (1.4)
2 days	50.6 (2.1)	29.8 (2.2)	30.3 (1.2)	30.2 (2.0)	44.9 (1.7)
3 days	49.8 (2.0)	29.0 (1.9)	29.2 (1.1)	30.8 (2.7)	44.9 (1.7)
1 week	47.8 (2.8)	29.0 (1.5)	29.3 (1.3)	30.0 (2.0)	43.6 (1.1)
2 weeks	45.2 (2.0)	27.4 (1.7)	27.7 (1.0)	28.4 (2.1)	42.8 (1.4)
3 weeks	44.8 (1.6)	26.1 (1.8)	26.4 (1.0)	27.0 (1.9)	42.3 (1.2)
1 month	45.7 (1.9)	26.9 (1.8)	27.2 (1.3)	27.8 (1.8)	42.5 (1.6)
2 months	46.6 (1.0)	25.5 (1.7)	25.8 (1.1)	27.4 (1.8)	41.0 (1.7)
4 months	47.0 (1.5)	24.1 (1.4)	25.2 (1.3)	26.8 (2.2)	44.1 (1.1)
6 months	45.7 (1.5)	24.1 (1.4)	24.3 (2.1)	25.2 (1.7)	43.3 (1.4)
1 year	46.2 (1.2)	21.0 (1.9)	22.0 (1.4)	24.2 (1.2)	45.6 (1.4)

Table 5.25 Shore A hardness for specimens stored in 50% ethanol at 37±1°C, mean (sd)

Test period	Liquid (50% ethanol)				
	Vertex™Soft	EverSoft®	Molloplast-B®	Ufi Gel SC	BE
Initial	50.7 (2.3)	25.6 (1.2)	32.6 (2.5)	24.3 (3.2)	44.6 (1.0)
0.5 hour	48.7 (2.5)	26.1 (1.0)	32.8 (2.7)	24.6 (3.2)	44.4 (0.6)
1 hour	43.1 (2.3)	24.1 (1.1)	31.8 (3.1)	23.9 (3.3)	45.6 (1.5)
2 hours	39.5 (1.7)	23.6 (1.4)	32.3 (2.4)	27.8 (2.9)	43.9 (0.9)
4 hours	33.6 (1.8)	20.7 (1.3)	31.6 (2.9)	24.6 (3.2)	46.2 (1.1)
6 hours	33.4 (2.2)	20.2 (1.3)	31.5 (2.6)	23.9 (2.9)	44.3 (0.7)
1 day	33.9 (1.7)	16.7 (1.7)	32.6 (2.8)	23.5 (3.6)	44.6 (1.1)
2 days	36.4 (1.3)	17.5 (1.6)	31.3 (2.9)	23.9 (3.0)	42.8 (1.5)
3 days	36.9 (2.2)	19.5 (1.3)	31.1 (3.0)	23.8 (3.5)	42.1 (1.7)
1 week	41.0 (2.4)	21.0 (1.7)	30.2 (2.8)	23.8 (3.1)	43.0 (0.6)
2 weeks	44.4 (3.6)	25.2 (1.3)	29.8 (2.7)	23.2 (2.7)	41.5 (1.0)
3 weeks	45.9 (4.6)	26.1 (0.9)	29.2 (3.0)	23.6 (2.3)	40.5 (1.7)
1 month	45.9 (4.7)	27.4 (1.4)	29.0 (2.9)	23.2 (2.1)	40.3 (1.7)
2 months	47.0 (4.8)	28.5 (3.5)	28.5 (2.8)	24.4 (3.3)	38.4 (0.7)
4 months	41.8 (4.5)	22.5 (3.2)	28.0 (3.0)	26.6 (1.7)	38.7 (1.4)
6 months	46.4 (4.0)	25.9 (3.1)	27.5 (2.5)	26.6 (2.6)	40.0 (2.4)
1 year	44.4 (5.9)	13.9 (4.5)	27.7 (2.5)	25.6 (1.9)	40.8 (2.3)

Table 5.26 Shore A hardness for specimens stored in coconut oil at 37±1°C, mean (sd)

Test period	Liquid (coconut oil)				
	Vertex™Soft	EverSoft®	Molloplast-B®	Ufi Gel SC	BE
Initial	47.5 (1.9)	29.3 (2.2)	35.1 (1.7)	25.4 (1.7)	44.1 (1.5)
0.5 hour	47.4 (1.4)	31.1 (2.1)	33.9 (1.4)	25.2 (1.8)	38.2 (1.9)
1 hour	45.4 (1.6)	30.6 (1.9)	32.6 (1.4)	23.6 (2.0)	38.0 (1.9)
2 hours	46.6 (1.5)	30.4 (2.2)	31.1 (1.6)	23.6 (2.4)	36.6 (2.0)
4 hours	47.5 (2.0)	31.0 (2.1)	30.3 (1.7)	23.4 (2.3)	35.4 (1.8)
6 hours	46.7 (1.7)	30.2 (1.9)	29.5 (1.5)	22.8 (2.6)	33.1 (1.8)
1 day	51.0 (1.9)	34.8 (1.5)	30.3 (1.6)	23.3 (2.3)	29.7 (2.1)
2 days	47.2 (1.6)	35.1 (1.8)	30.0 (1.5)	23.0 (2.3)	28.2 (2.3)
3 days	50.2 (1.4)	38.7 (1.8)	30.6 (1.9)	23.6 (2.5)	28.4 (2.6)
1 week	52.0 (2.0)	43.6 (2.0)	31.0 (1.6)	23.3 (2.3)	25.9 (2.7)
2 weeks	55.2 (1.5)	49.0 (2.1)	31.5 (2.0)	24.9 (2.6)	27.7 (2.5)
3 weeks	56.1 (2.2)	56.1 (2.2)	31.3 (1.5)	24.8 (2.1)	26.9 (2.3)
1 month	59.3 (1.9)	63.4 (1.6)	30.5 (2.0)	23.3 (2.3)	28.5 (2.0)
2 months	72.6 (2.2)	81.1 (2.6)	30.7 (1.6)	23.6 (2.1)	27.0 (2.1)
4 months	76.9 (1.2)	85.6 (1.7)	31.8 (1.4)	24.9 (2.7)	30.3 (2.1)
6 months	82.6 (2.2)	87.4 (2.4)	31.0 (1.6)	24.8 (2.0)	27.7 (3.0)
1 year	85.6 (1.6)	87.2 (3.3)	31.6 (1.7)	25.2 (1.9)	16.4 (3.5)

Table 5.27 Shore A hardness for specimens stored in HB307 at 37±1°C, mean (sd)

Test period	Liquid (HB307)				
	Vertex™Soft	EverSoft®	Molloplast-B®	Ufi Gel SC	BE
Initial	51.3 (1.7)	33.0 (2.5)	35.2 (2.0)	23.0 (1.2)	44.6 (2.5)
0.5 hour	48.2 (2.0)	34.3 (2.4)	34.4 (2.1)	22.3 (1.3)	35.7 (2.4)
1 hour	47.7 (1.4)	32.5 (2.4)	33.9 (2.2)	21.1 (1.4)	34.6 (2.3)
2 hours	45.9 (2.2)	31.3 (2.3)	32.8 (2.0)	20.5 (1.2)	33.9 (2.1)
4 hours	47.4 (1.7)	33.1 (1.4)	31.0 (2.2)	21.0 (1.1)	32.0 (2.0)
6 hours	49.0 (1.8)	32.6 (2.3)	32.1 (1.9)	20.5 (1.3)	32.1 (2.2)
1 day	49.3 (1.7)	34.9 (2.0)	30.2 (1.1)	20.7 (1.3)	26.1 (2.3)
2 days	53.6 (2.2)	31.3 (2.9)	31.3 (2.0)	19.5 (1.5)	22.1 (2.7)
3 days	57.9 (2.1)	30.8 (2.9)	30.8 (2.0)	20.8 (1.6)	25.2 (3.1)
1 week	58.0 (2.0)	30.2 (2.5)	30.2 (2.0)	21.1 (1.3)	23.8 (2.6)
2 weeks	57.7 (1.9)	29.3 (2.9)	29.3 (1.9)	20.8 (1.7)	24.4 (3.5)
3 weeks	59.7 (2.1)	29.7 (2.3)	29.7 (2.1)	22.0 (1.8)	24.6 (2.3)
1 month	64.8 (1.4)	71.3 (2.3)	30.2 (2.0)	20.0 (1.5)	23.9 (1.8)
2 months	66.6 (1.3)	75.2 (1.5)	30.7 (2.0)	20.2 (1.1)	18.6 (3.6)
4 months	71.5 (1.5)	77.4 (3.1)	29.7 (2.0)	22.6 (1.7)	Not tested
6 months	76.1 (1.7)	79.0 (3.0)	30.5 (1.9)	21.1 (1.9)	Not tested
1 year	83.0 (1.7)	79.8 (3.6)	31.3 (2.3)	23.1 (1.3)	Not tested

5.2.2 Shore A hardness in relation to Young's modulus

Tables 5.28-29 give the Shore A hardness initially and at one year to demonstrate the change in hardness and corresponding Young's modulus. As processed, VT had the greatest Shore A hardness value, followed by BE, MB, UG and ES being the more compliant materials. In Table 5.28, VT, ES and BE in oils and VT and ES in 3AA exhibited the greatest Shore A hardness change (significant difference, $P<0.05$) by the end of one year, the rank order (absolute value) of Shore A hardness change for materials in food simulating liquids were ES in CO > ES in HB > VT in CO > VT in HB > BE in CO > BE in HB > ES in 3AA > VT in 3AA > ES in 50E (Table 5.28).

Table 5.28 Comparison of initial and final apparent Shore A hardness of denture soft lining materials following storage for one year, mean (standard deviation).

Materials	In DW @ 37°C			In AS @ 37°C		
	Initial Hardness	Final Hardness at one year	Hardness Change	Initial Hardness	Final Hardness at one year	Hardness Change
VT	53.7 (2.2)	47.2 (2.6)	**-6.5**	49.1 (2.4)	53.9 (4.3)	**4.8**
ES	31.0 (1.9)	24.2 (1.8)	**-6.8**	28.7 (3.1)	32.5 (3.0)	**3.8**
MB	31.6 (2.1)	25.7 (2.3)	**-5.9**	28.2 (2.0)	31.3 (1.4)	**3.1**
UG	31.3 (3.4)	26.4 (2.7)	**-4.9**	27.7 (1.5)	30.3 (2.5)	**2.6**
BE	41.0 (1.8)	42.7 (2.2)	**1.7**	42.8 (1.9)	44.8 (1.8)	**2.0**

Materials	In 3AA @ 37°C			In 10E @ 37°C		
	Initial Hardness	Final Hardness @ 1 year	Hardness Change	Initial Hardness	Final Hardness @ 1 year	Hardness Change
VT	53.1 (3.1)	40.5 (2.6)	**-12.6**	48.9 (2.0)	46.2 (1.2)	**-2.7**
ES	29.3 (2.5)	12.9 (2.8)	**-16.4**	29.3 (2.0)	21.0 (1.9)	**-8.3**
MB	35.9 (0.9)	32.5 (0.7)	**-3.4**	29.3 (0.9)	22.0 (1.4)	**-7.3**
UG	27.7 (2.3)	29.0 (4.0)	**1.3**	30.3 (1.7)	24.2 (1.2)	**-6.1**
BE	42.5 (2.0)	36.9 (2.3)	**-5.6**	43.6 (1.7)	45.4 (1.4)	**1.8**

Materials	In 50E @ 37°C			In CO @ 37°C		
	Initial Hardness	Final Hardness @ 1 year	Hardness Change	Initial Hardness	Final Hardness @ 1 year	Hardness Change
VT	50.7 (2.3)	44.4 (5.9)	**-6.3**	47.5 (1.9)	85.6 (1.6)	**38.1**
ES	25.6 (1.2)	13.9 (4.5)	**-11.7**	29.3 (2.2)	87.2 (3.3)	**57.9**
MB	32.6 (2.5)	27.7 (2.5)	**-4.9**	35.1 (1.7)	31.6 (1.7)	**-3.4**
UG	24.3 (3.2)	25.6 (1.9)	**1.3**	25.4 (1.7)	25.2 (1.9)	**-0.2**
BE	44.6 (1.0)	40.8 (2.3)	**-3.8**	44.1 (1.5)	16.4 (3.5)	**-27.7**

Materials	In HB @ 37°C		
	Initial Hardness	Final Hardness @ 1 year	Hardness Change
VT	51.3 (1.7)	83.0 (1.7)	**31.7**
ES	33.0 (2.5)	79.8 (3.6)	**46.8**
MB	35.2 (2.0)	31.3 (2.3)	**-3.9**
UG	23.0 (1.2)	23.1 (1.3)	**0.1**
BE	44.6 (2.5)	*18.6 (3.6)	**-26.0**

* The specimens in HB307 had completely disintegrated by 4 months so the final data is at 2 months.

In Table 5.29, for all four materials except BE, the Young's modulus decreased with respect to time in DW and 10E. In all materials, except UG, the Young's modulus decreased with respect to time in 3AA and 50E. For methacrylate-based denture soft lining materials, unlike silicone-based denture soft lining materials, the Young's modulus increased markedly with respect to time in CO and HB. For BE, the Young's modulus decreased markedly with respect to time in CO and HB.

Table 5.29 Comparison of initial and final Young's modulus following storage for one year, mean (standard deviation).

Materials	Young's Modulus (E) / DW (MPa)			Young's Modulus (E) / AS (MPa)		
	Initial	Final @ 1 year	Change	Initial	Final @ 1 year	Change
VT	2.84 (0.21)	2.22 (0.22)	**-0.62**	2.38 (0.28)	2.86 (0.33)	**0.48**
ES	1.19 (0.20)	0.89 (0.20)	**-0.30**	1.09 (0.28)	1.27 (0.28)	**0.18**
MB	1.22 (0.21)	0.96 (0.21)	**-0.28**	1.06 (0.24)	1.21 (0.21)	**0.15**
UG	1.21 (0.24)	0.99 (0.27)	**-0.22**	1.04 (0.22)	1.16 (0.26)	**0.12**
BE	1.76 (0.23)	1.88 (0.24)	**0.12**	1.88 (0.23)	2.03 (0.23)	**0.15**

Materials	Young's Modulus (E) / 3AA (MPa)			Young's Modulus (E) / 10E (MPa)		
	Initial	Final @ 1 year	Change	Initial	Final @ 1 year	Change
VT	2.77 (0.28)	1.73 (0.26)	**-1.04**	2.37 (0.24)	2.14 (0.20)	**-0.23**
ES	1.11 (0.26)	0.50 (0.27)	**-0.61**	1.11 (0.24)	0.77 (0.23)	**-0.34**
MB	1.45 (0.19)	1.27 (0.18)	**-0.18**	1.11 (0.19)	0.81 (0.21)	**-0.20**
UG	1.04 (0.25)	1.10 (0.32)	**0.06**	1.16 (0.22)	0.89 (0.21)	**-0.27**
BE	1.86 (0.23)	1.51 (0.24)	**-0.35**	1.94 (0.22)	2.08 (0.21)	**0.14**

Materials	Young's Modulus (E) / 50E (MPa)			Young's Modulus (E) / CO (MPa)		
	Initial	Final @ 1 year	Change	Initial	Final @ 1 year	Change
VT	2.53 (0.25)	2.00 (0.40)	**-0.53**	2.25 (0.23)	13.88 (0.22)	**11.53**
ES	0.95 (0.20)	0.53 (0.34)	**-0.42**	1.11 (0.24)	15.89 (0.29)	**14.78**
MB	1.27 (0.26)	1.04 (0.27)	**-0.23**	1.40 (0.22)	1.22 (0.22)	**-0.18**
UG	0.90 (0.28)	0.95 (0.23)	**0.05**	0.94 (0.22)	0.94 (0.29)	**0.00**
BE	2.02 (0.20)	1.75 (0.25)	**0.27**	1.98 (0.22)	0.61 (0.30)	**-1.37**

Materials	Young's Modulus (E) / HB (MPa)		
	Initial	Final @ 1 year	Change
VT	2.59 (0.22)	11.43 (0.22)	**8.84**
ES	1.29 (0.25)	9.28 (0.23)	**7.89**
MB	1.41 (0.23)	1.21 (0.25)	**-0.20**
UG	0.85 (0.21)	0.85 (0.27)	**0.00**
BE	2.02 (0.26)	0.68 (0.19)	**-1.34**

* The specimens in HB had completely disintegrated by 4 months so the final Young's modulus data is at month 2.

5.3 Surface roughness evaluation

Food simulating liquids affected the specimens of both methacrylate-based and silicone-based denture soft lining materials. Figures 5.43-54 show the age change in surface roughness of four commercial denture soft lining material caused by seven immersing liquids. Increasing surface roughness was seen for ES in all liquids except in oils.

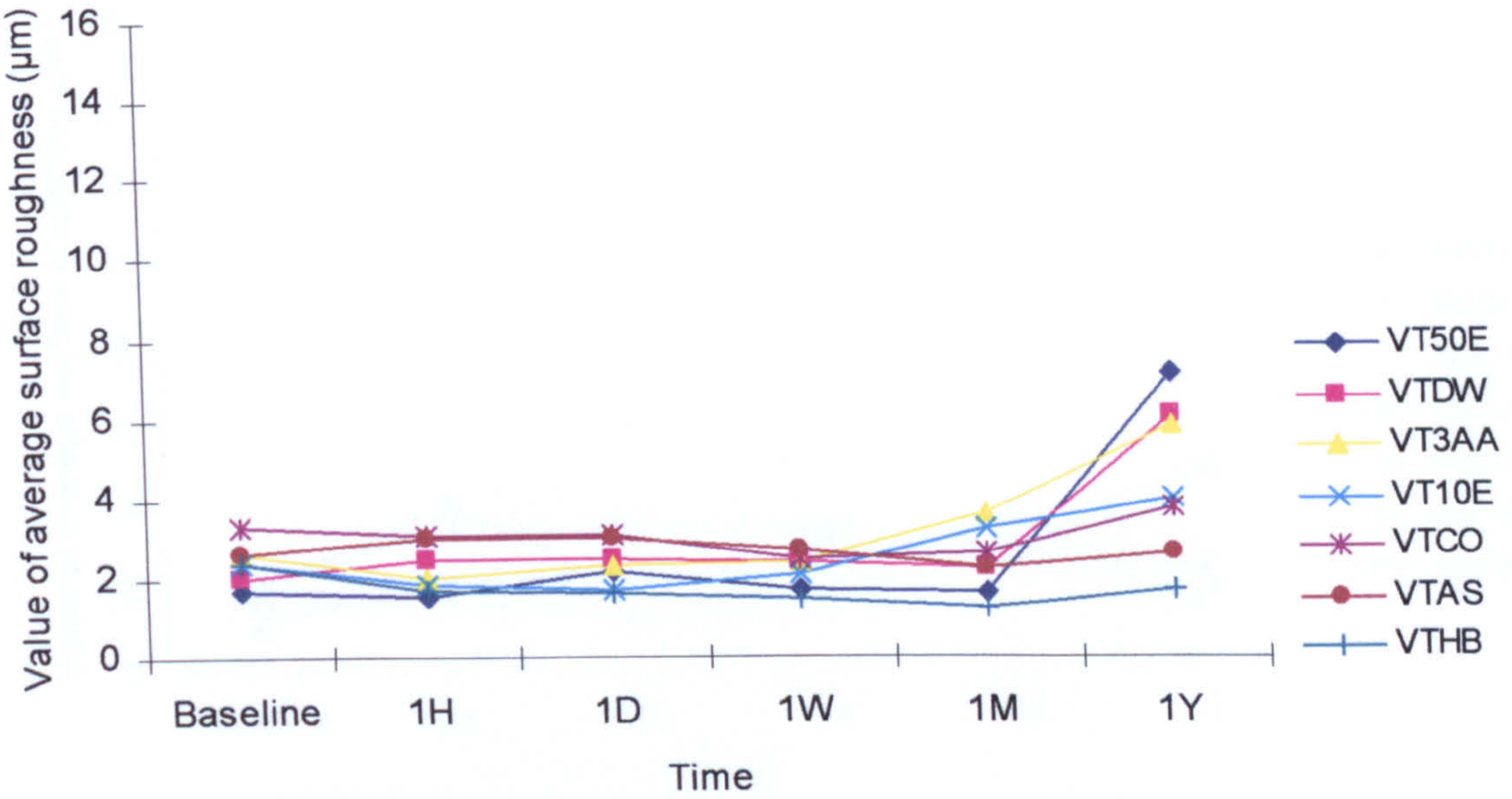


Figure 5.43 Age change of average surface roughness of Vertex™Soft (VT) samples, which were immersed in distilled water (DW), artificial saliva (AS), 3% acetic acid (3AA), 10% ethanol (10E), 50% ethanol (50E), coconut oil (CO) and HB307 (HB).

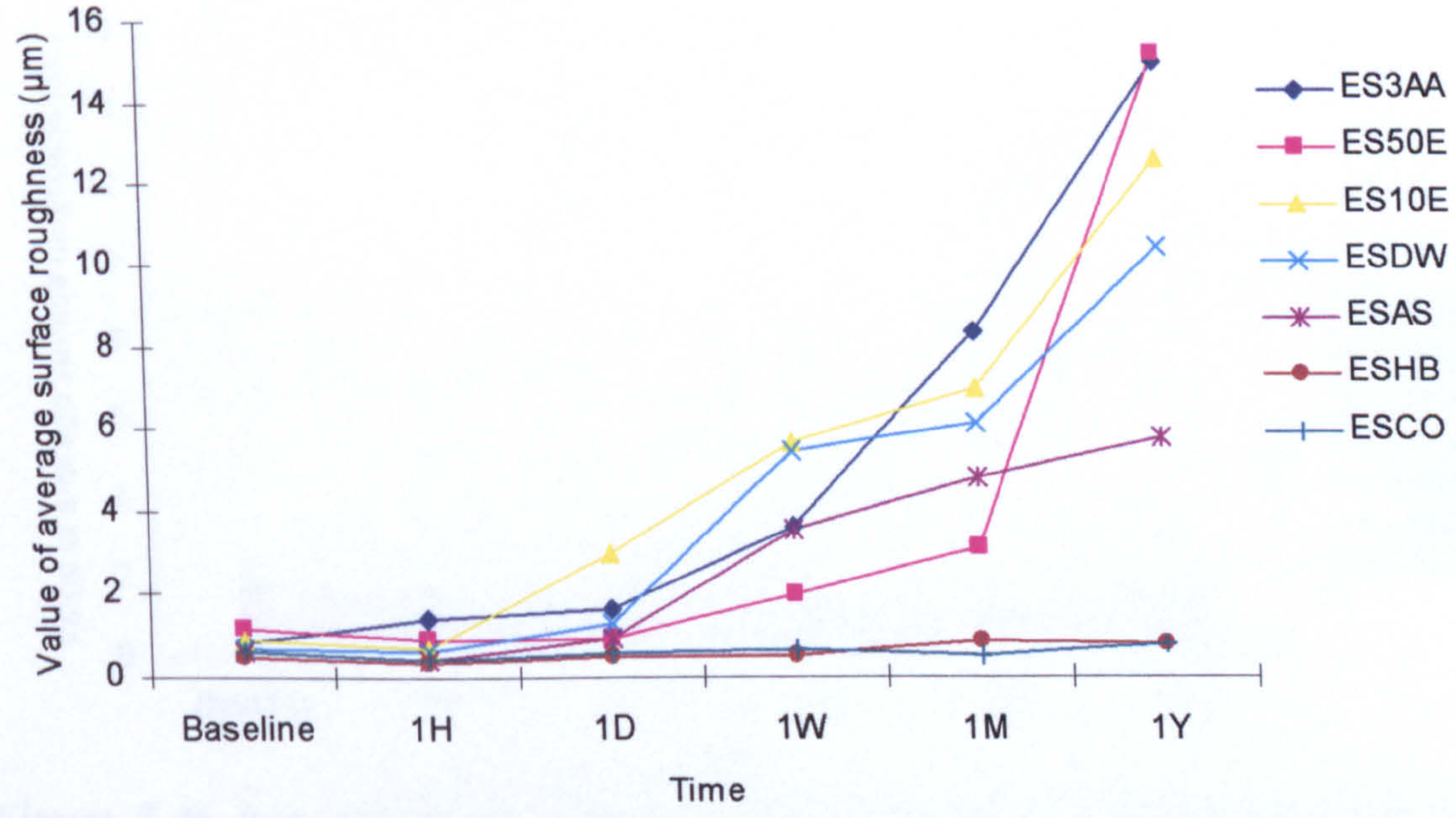


Figure 5.44 Age change of average surface roughness of EverSoft® (ES) samples, which were immersed in distilled water (DW), artificial saliva (AS), 3% acetic acid (3AA), 10% ethanol (10E), 50% ethanol (50E), coconut oil (CO) and HB307 (HB).

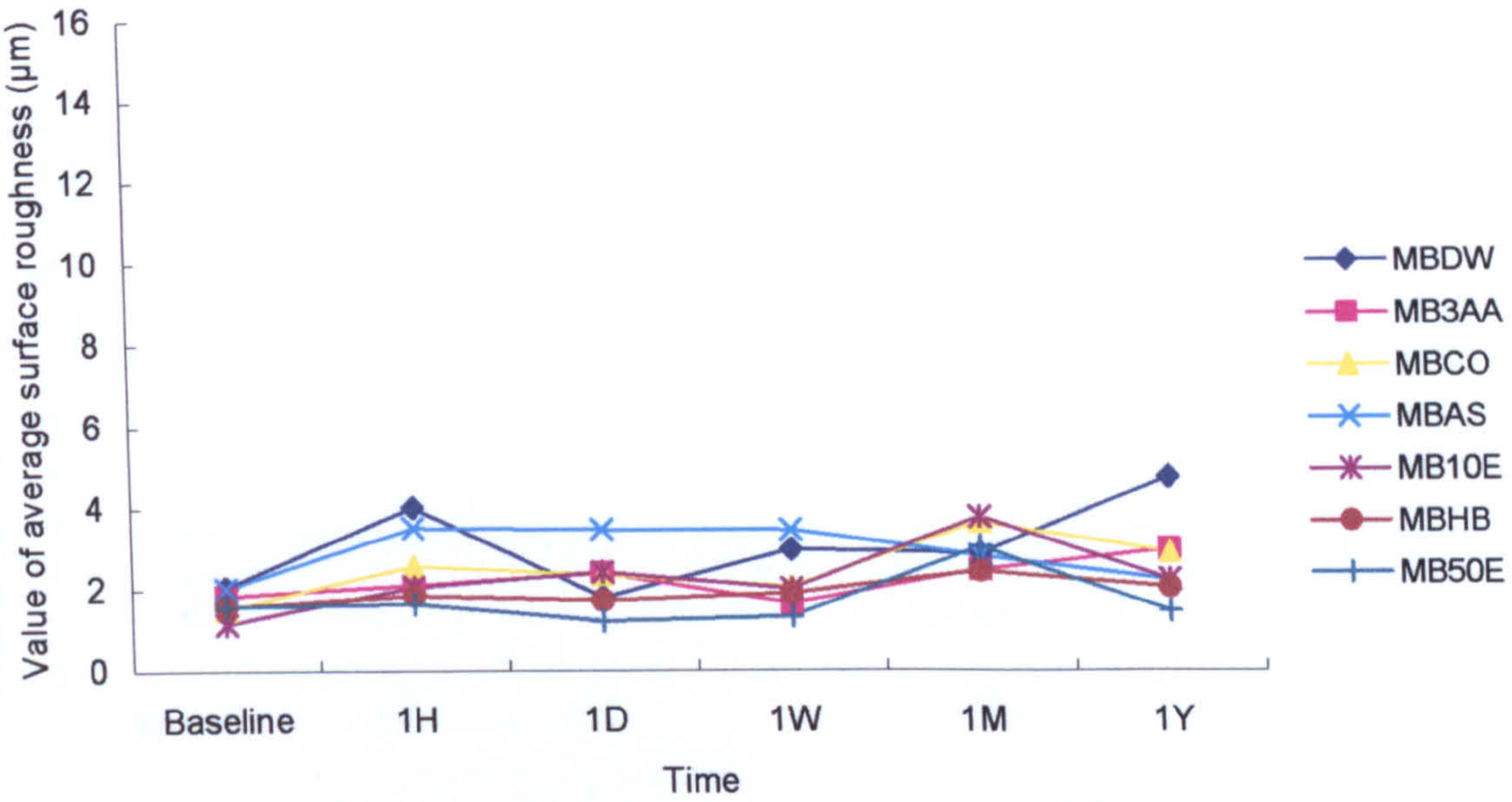


Figure 5.45 Age change of average surface roughness of Molloplast-B® (MB) samples, which were immersed in distilled water (DW), artificial saliva (AS), 3% acetic acid (3AA), 10% ethanol (10E), 50% ethanol (50E), coconut oil (CO) and HB307 (HB).

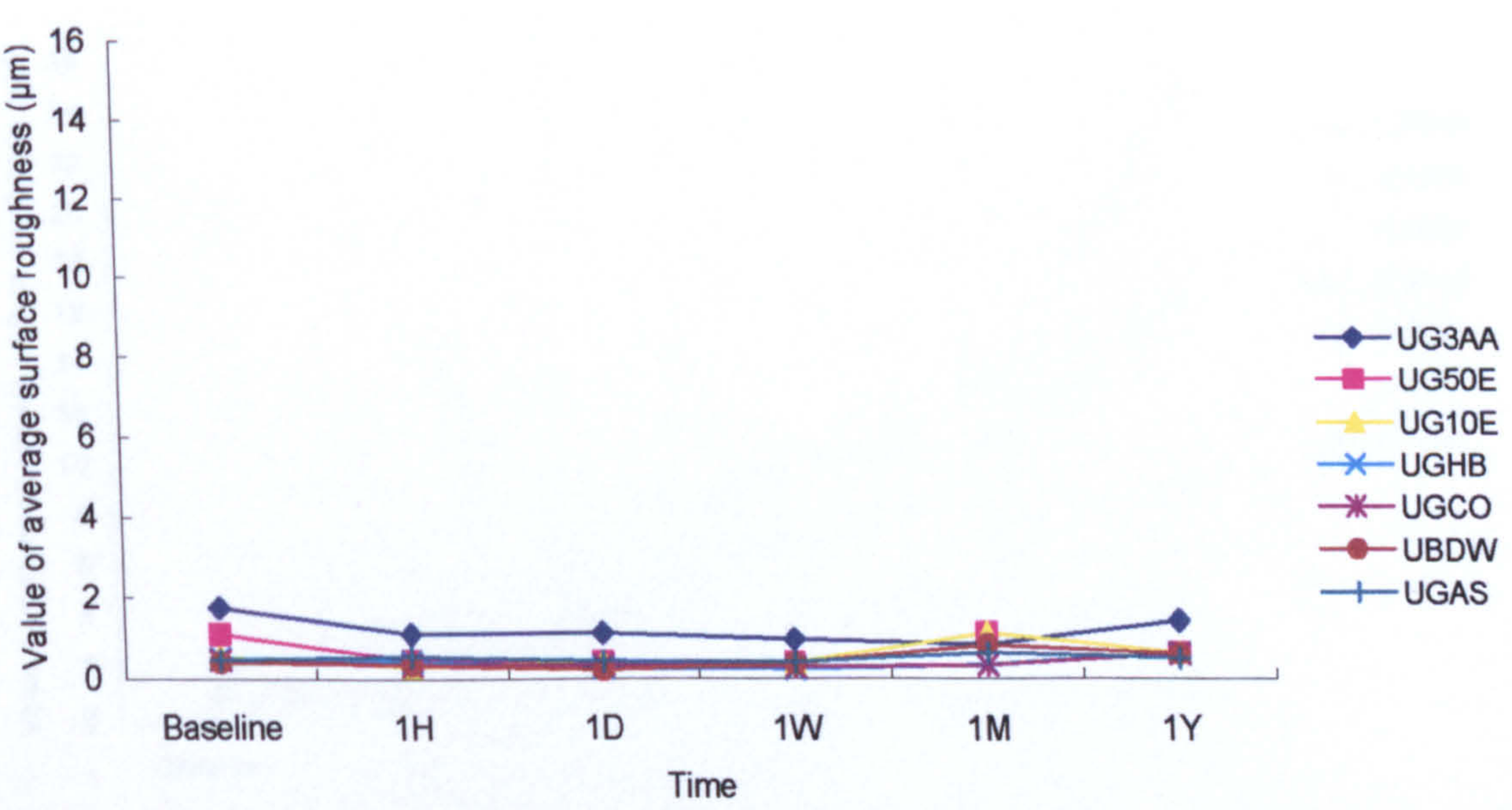


Figure 5.46 Age change of average surface roughness of Ufi Gel SC (UG) samples, which were immersed in distilled water (DW), artificial saliva (AS), 3% acetic acid (3AA), 10% ethanol (10E), 50% ethanol (50E), coconut oil (CO) and HB307 (HB).

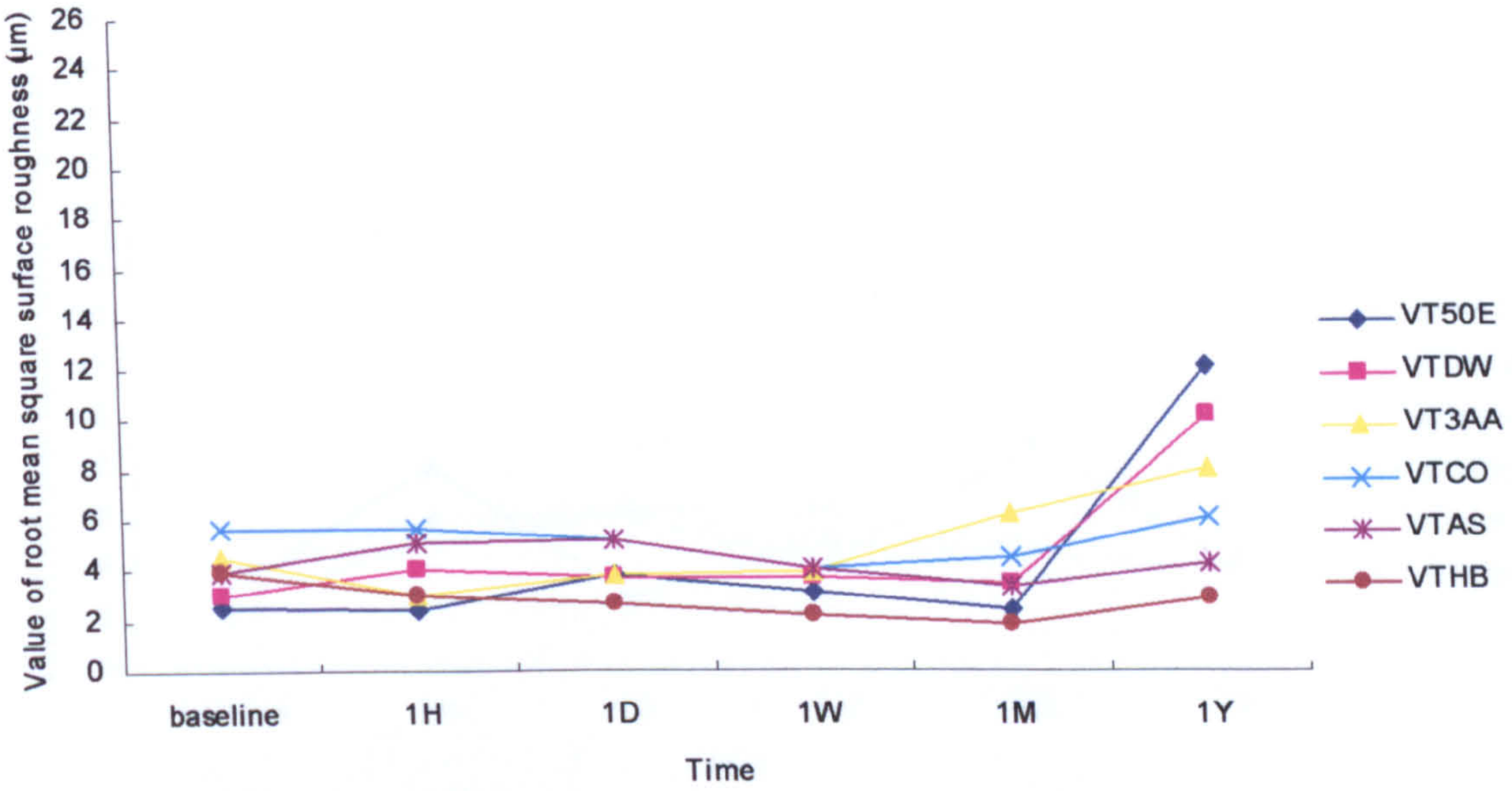


Figure 5.47 Age change of root mean square surface roughness of Vertex™Soft (VT) samples, which were immersed in distilled water (DW), artificial saliva (AS), 3% acetic acid (3AA), 10% ethanol (10E), 50% ethanol (50E), coconut oil (CO) and HB307 (HB).

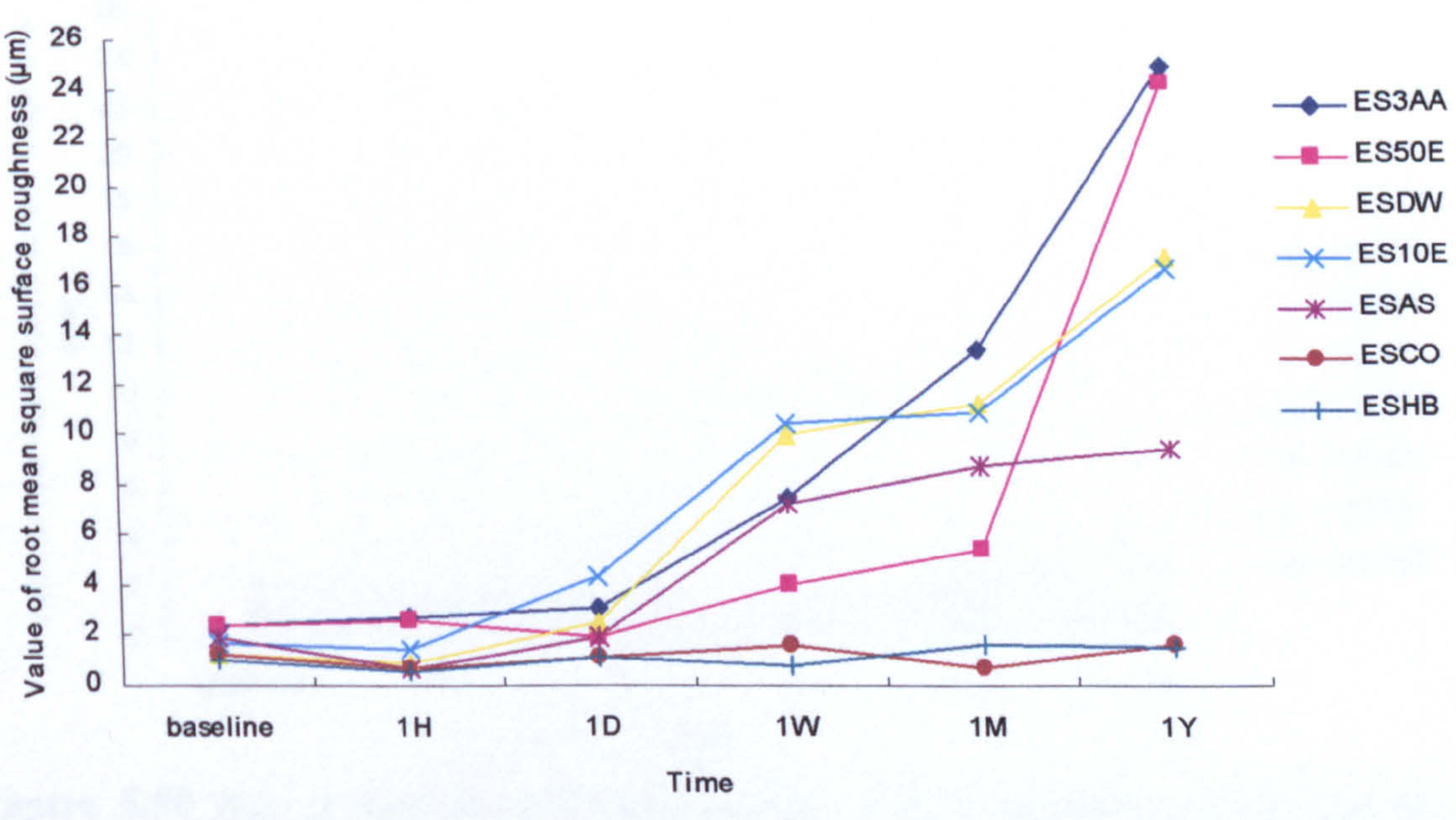


Figure 5.48 Age change of root mean square surface roughness of EverSoft® (ES) samples, which were immersed in distilled water (DW), artificial saliva (AS), 3% acetic acid (3AA), 10% ethanol (10E), 50% ethanol (50E), coconut oil (CO) and HB307 (HB).

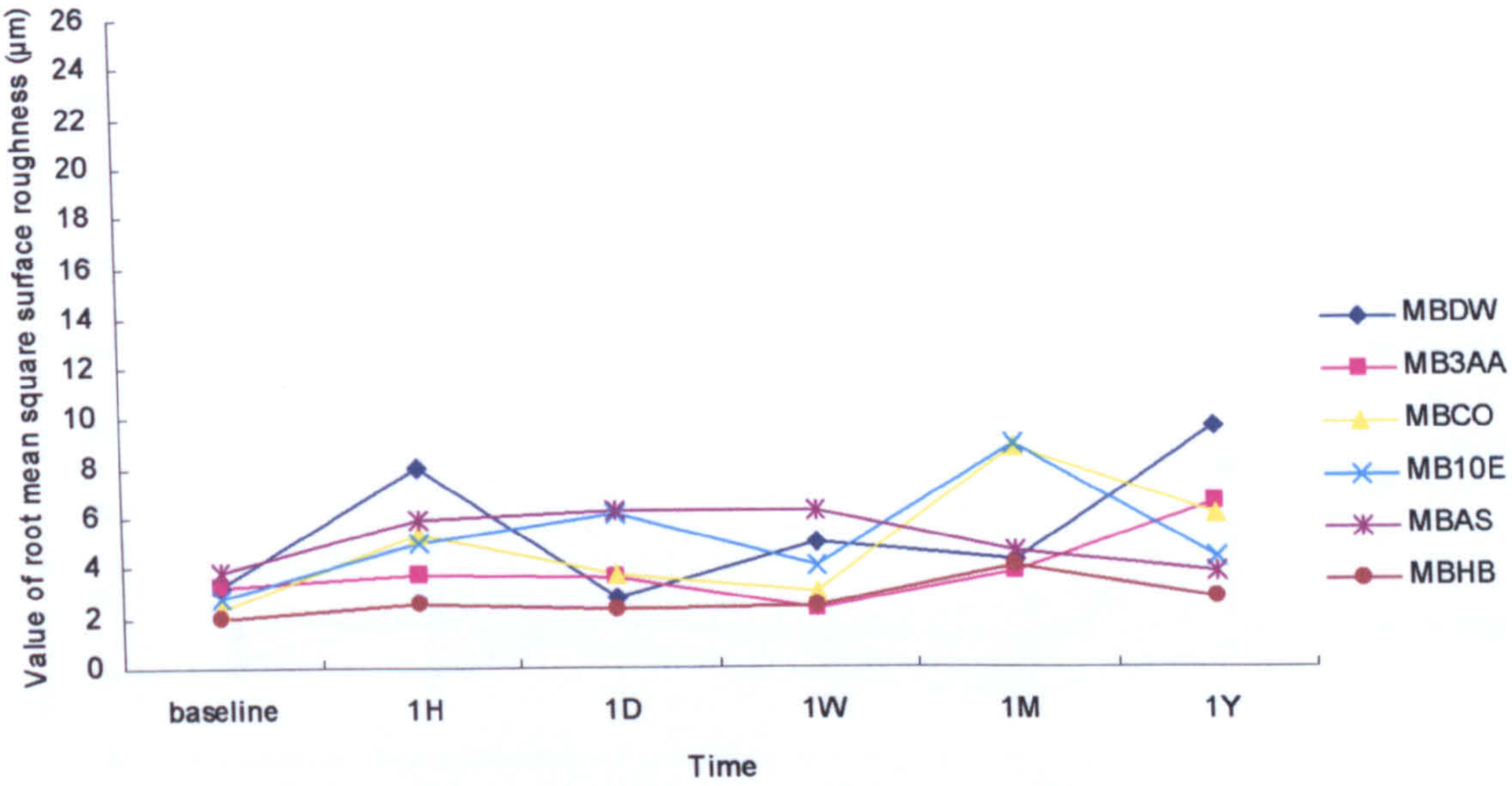


Figure 5.49 Age change of root mean square surface roughness of Molloplast-B® (MB) samples, which were immersed in distilled water (DW), artificial saliva (AS), 3% acetic acid (3AA), 10% ethanol (10E), 50% ethanol (50E), coconut oil (CO) and HB307 (HB).

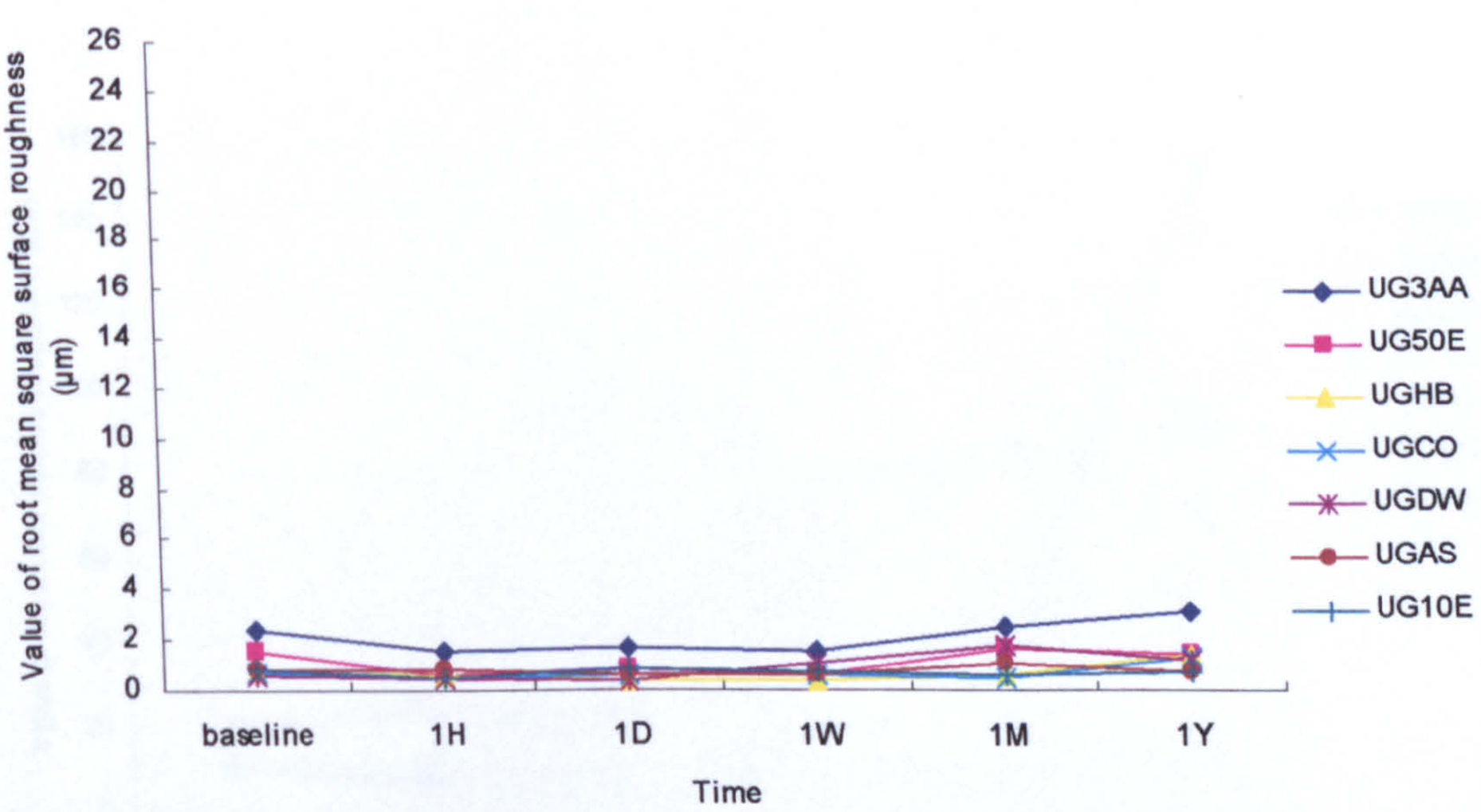


Figure 5.50 Age change of root mean square surface roughness of Ufi Gel SC (UG) samples, which were immersed in distilled water (DW), artificial saliva (AS), 3% acetic acid (3AA), 10% ethanol (10E), 50% ethanol (50E), coconut oil (CO) and HB307 (HB).

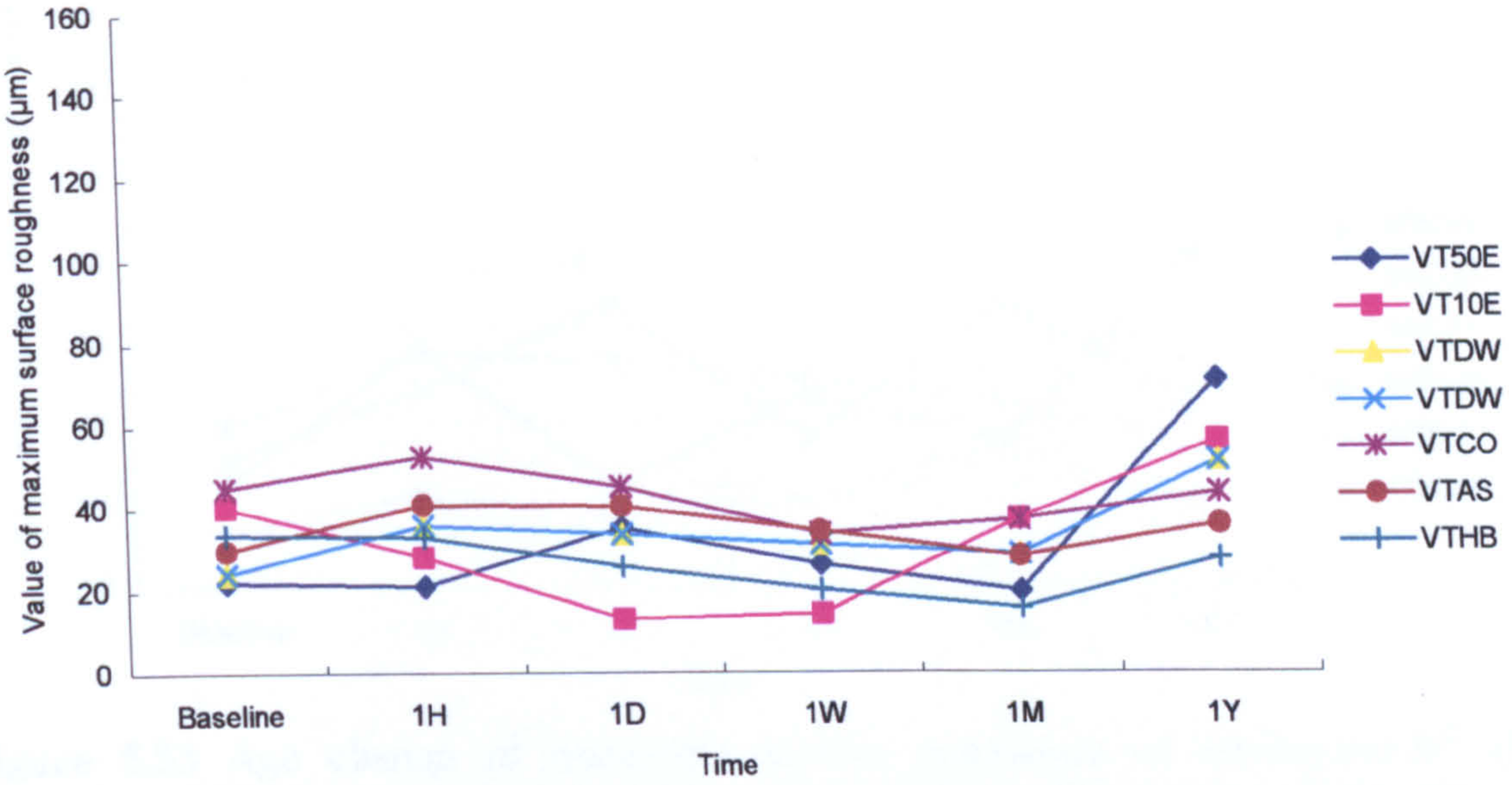


Figure 5.51 Age change of maximum surface roughness of Vertex™Soft (VT) samples, which were immersed in distilled water (DW), artificial saliva (AS), 3% acetic acid (3AA), 10% ethanol (10E), 50% ethanol (50E), coconut oil (CO) and HB307 (HB).

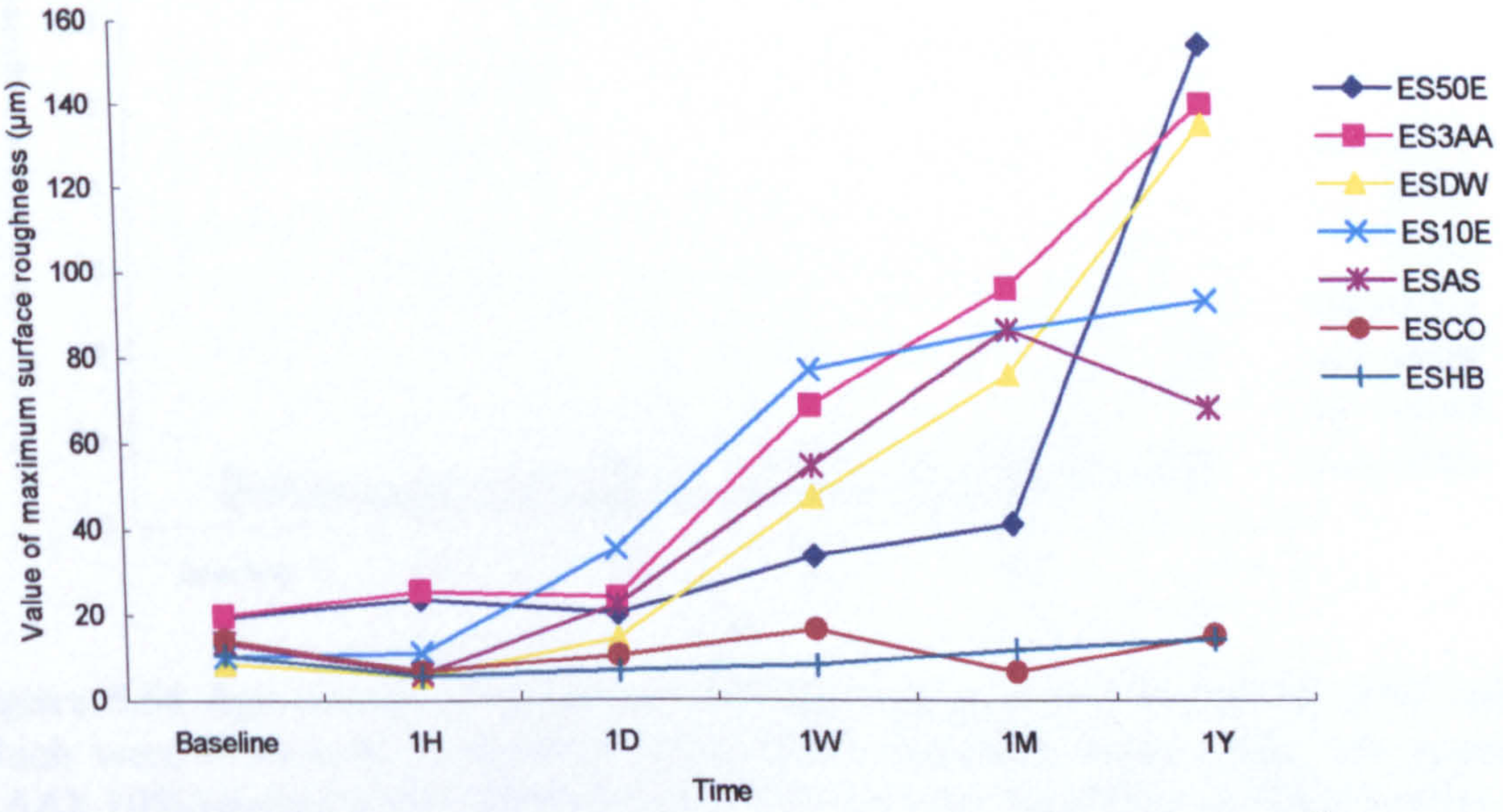


Figure 5.52 Age change of maximum surface roughness of EverSoft® (ES) samples, which were immersed in distilled water (DW), artificial saliva (AS), 3% acetic acid (3AA), 10% ethanol (10E), 50% ethanol (50E), coconut oil (CO) and HB307 (HB).

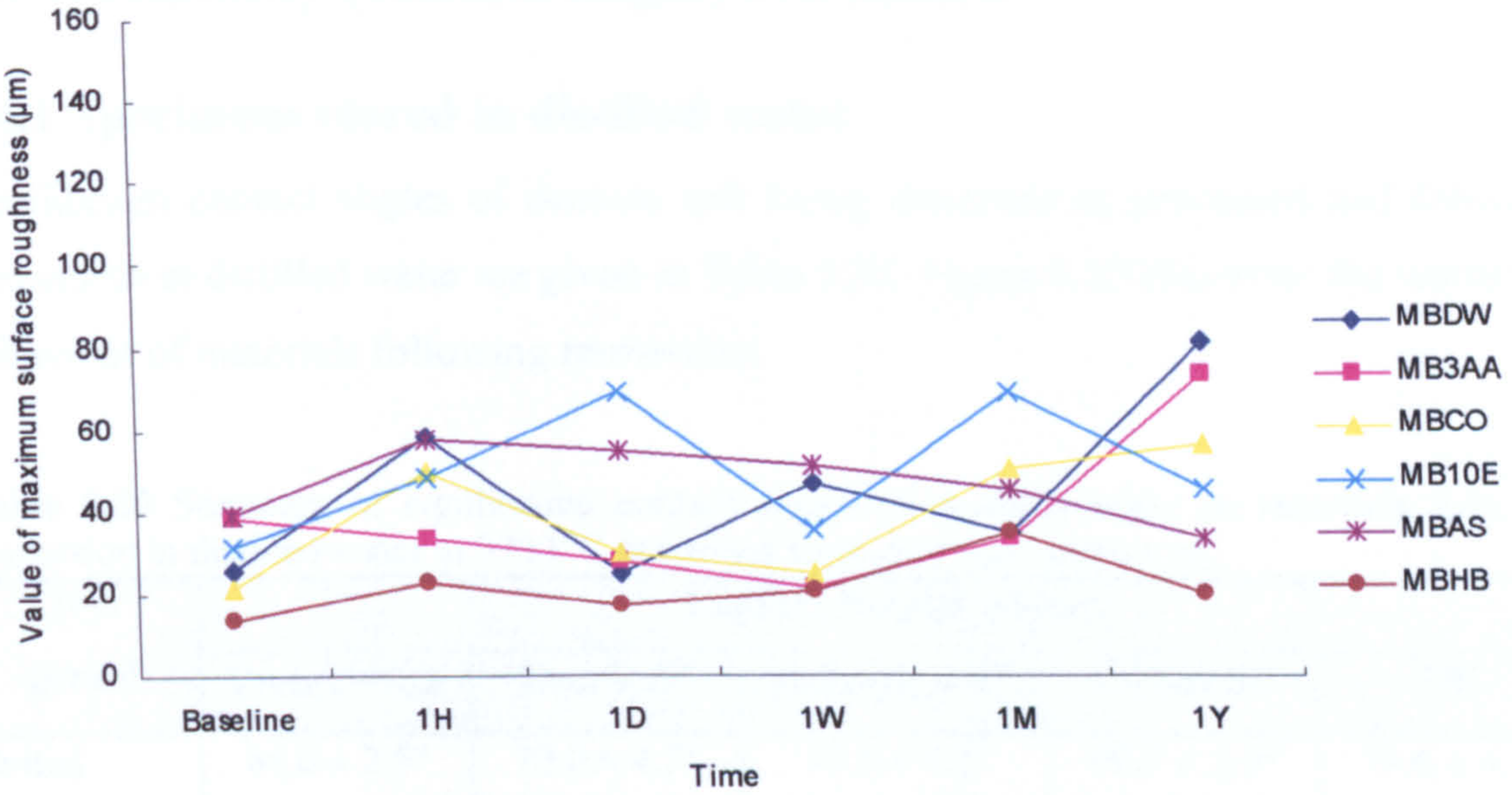


Figure 5.53 Age change of maximum surface roughness of Molloplast-B® (MB) samples, which were immersed in distilled water (DW), artificial saliva (AS), 3% acetic acid (3AA), 10% ethanol (10E), 50% ethanol (50E), coconut oil (CO) and HB307 (HB).

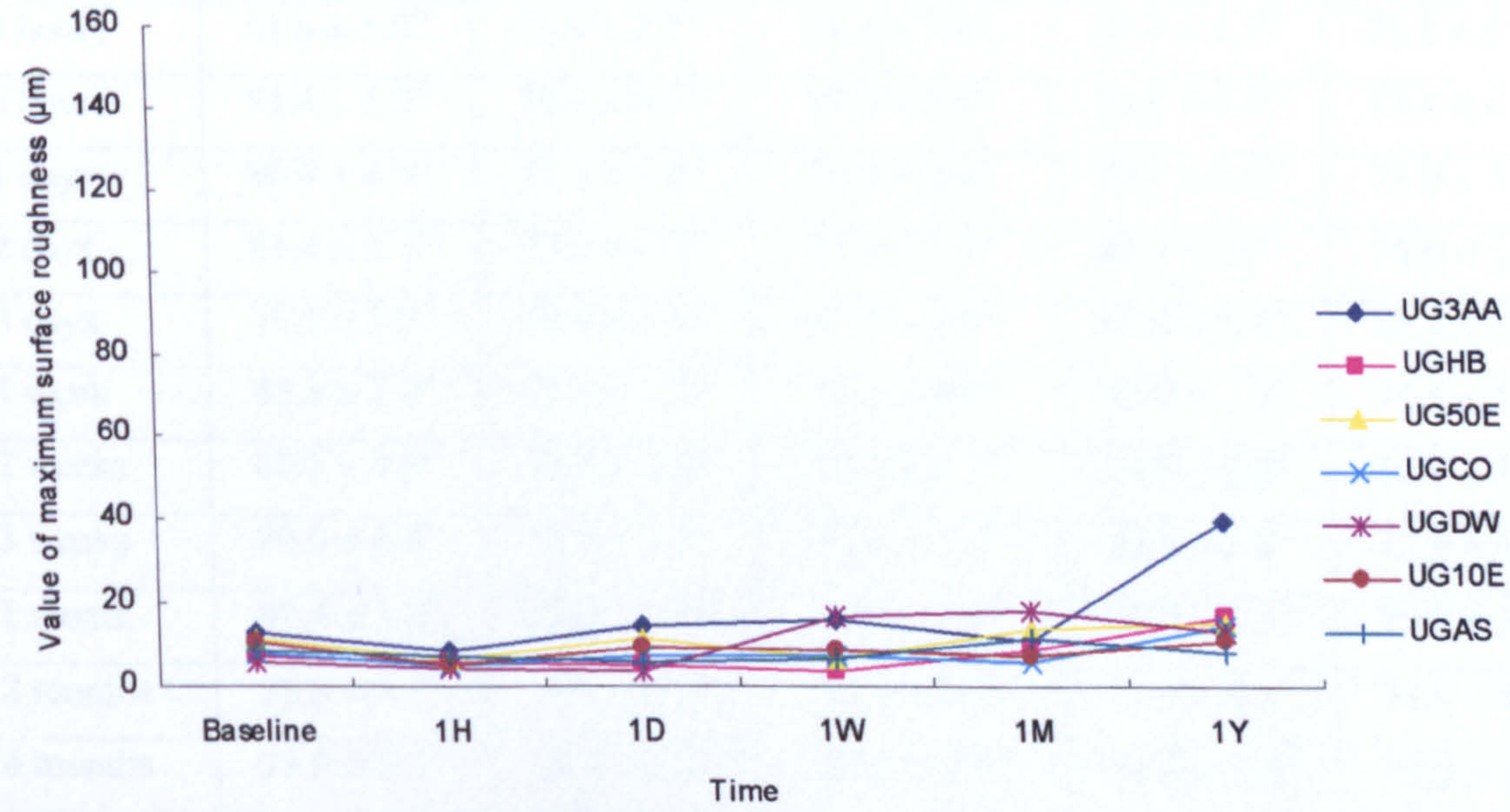


Figure 5.54 Age change of maximum surface roughness of Ufi Gel SC (UG) samples, which were immersed in distilled water (DW), artificial saliva (AS), 3% acetic acid (3AA), 10% ethanol (10E), 50% ethanol (50E), coconut oil (CO) and HB307 (HB).

Changes in the surface roughness of the materials varied depending upon both immersion time and types of immersing liquids. Severe changes in surface porosity were observed with ES. A significant correlation between surface roughness and immersion time was observed with ES.

5.4 Wettability (contact angle) evaluation

5.4.1 Specimens stored in distilled water

Equilibrium contact angles of denture soft lining materials as processed and following immersion in distilled water are given in Table 5.30. Figure 5.55 illustrates the wettability behaviour of materials following immersion.

Table 5.30 Summary of equilibrium contact angles of distilled water on materials following immersion in distilled water at 37±1°C at various time intervals, mean ± sd

Test period	Liquid (distilled water)				
	Vertex™Soft	EverSoft®	Molloplast-B®	Ufi Gel SC	BE
Initial	84.0 ± 2.5°	73.0 ± 4.5°	89.5 ± 4.2°	90.7 ± 2.9°	78.6 ± 4.4°
0.5 hour	84.3 ± 2.9°	74.6 ± 5.1°	91.9 ± 4.8°	92.3 ± 1.9°	79.5 ± 5.3°
1 hour	83.3 ± 3.1°	74.5 ± 3.5°	86.3 ± 1.6°	89.6 ± 1.6°	76.8 ± 4.7°
2 hours	82.9 ± 2.8°	74.3 ± 4.0°	86.3 ± 1.9°	88.4 ± 2.9°	76.4 ± 4.9°
4 hours	81.6 ± 5.0°	73.9 ± 2.5°	86.4 ± 3.0°	87.1 ± 2.1°	74.3 ± 2.1°
6 hours	81.4 ± 4.0°	74.6 ± 6.3°	87.0 ± 2.4°	86.6 ± 3.7°	73.4 ± 4.4°
1 day	80.9 ± 4.0°	73.1 ± 2.8°	90.0 ± 3.4°	87.7 ± 5.6°	73.3 ± 3.0°
2 days	81.4 ± 3.1°	73.0 ± 4.7°	87.4 ± 2.7°	87.1 ± 2.7°	74.6 ± 5.0°
3 days	79.9 ± 2.5°	73.9 ± 3.9°	87.7 ± 4.0°	89.6 ± 5.4°	74.8 ± 3.1°
1 week	83.3 ± 1.4°	75.4 ± 1.4°	86.5 ± 2.4°	87.9 ± 2.5°	74.5 ± 5.7°
2 weeks	80.7 ± 3.8°	76.6 ± 3.8°	87.3 ± 3.3°	89.8 ± 5.2°	74.9 ± 3.8°
3 weeks	80.6 ± 4.4°	78.8 ± 3.3°	87.0 ± 1.2°	87.8 ± 2.6°	75.4 ± 4.4°
1 month	80.4 ± 5.2°	78.5 ± 5.4°	87.3 ± 2.8°	88.9 ± 5.3°	75.7 ± 5.3°
2 months	78.5 ± 5.1°	78.6 ± 4.1°	88.0 ± 3.2°	87.4 ± 4.1°	74.9 ± 4.7°
4 months	78.0 ± 2.4°	79.1 ± 2.2°	87.7 ± 2.9°	88.4 ± 5.4°	74.3 ± 4.4°
6 months	78.2 ± 3.7°	78.3 ± 3.8°	87.7 ± 2.9°	88.3 ± 4.4°	74.8 ± 2.2°
1 year	77.8 ± 4.6°	79.8 ± 3.4°	88.2 ± 2.6°	88.2 ± 5.4°	73.7 ± 4.6°

Following immersion in distilled water at 37±1°C for one year, MB, UG and BE showed little change in contact angle with time. VT became more wettable with time, but ES became less wettable with time. Meanwhile, the equilibrium contact angles between distilled water and MB and UG were significantly greater than on VT, ES and BE.

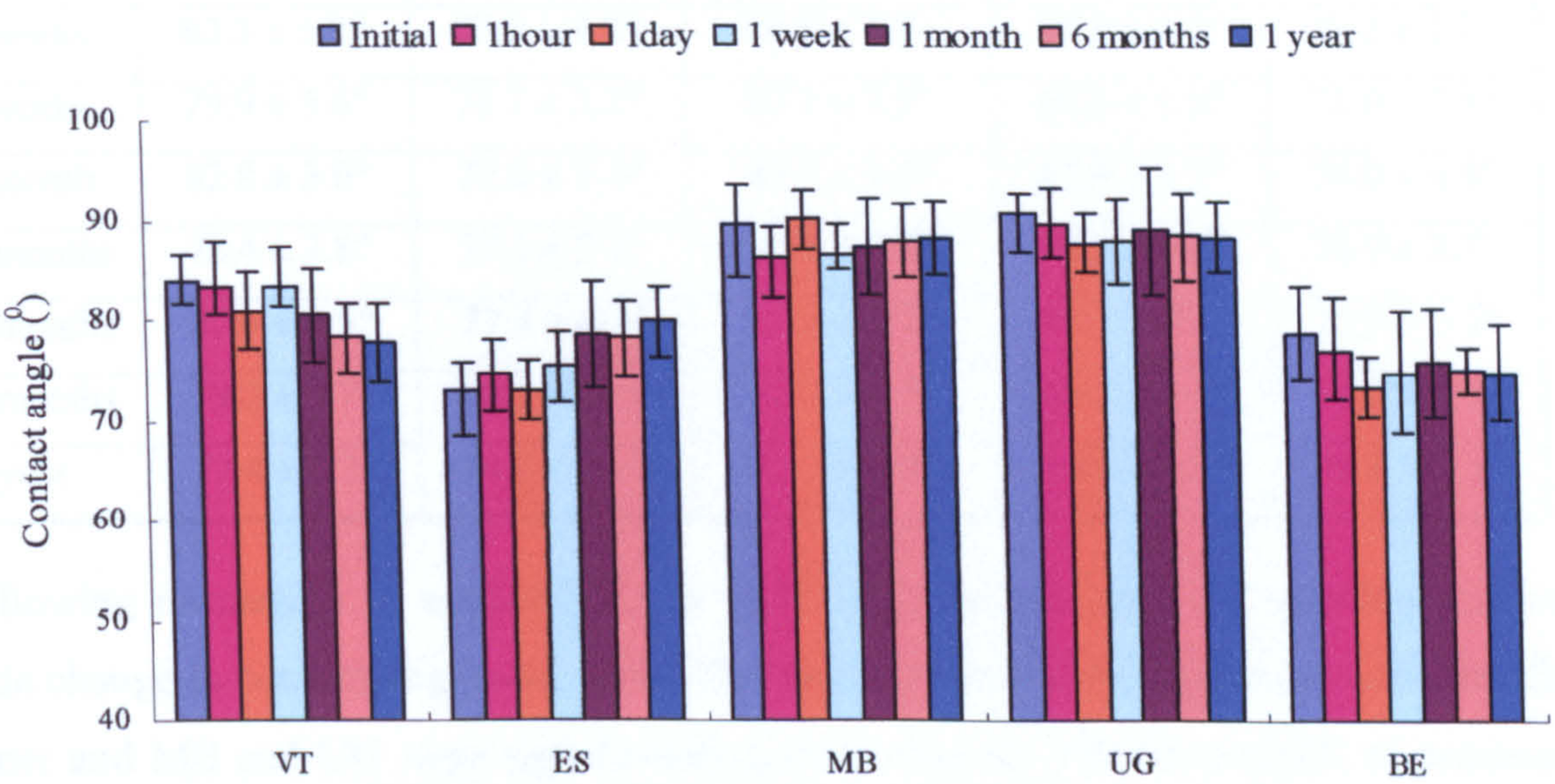


Figure 5.55 Equilibrium contact angles versus materials following immersion in distilled water.

5.4.2 Specimens stored in artificial saliva

Equilibrium contact angles of distilled water on denture soft lining materials as processed and following immersion in artificial saliva are given in Table 5.31. Figure 5.56 illustrates the wettability behaviour of materials following immersion.

Table 5.31 Summary of equilibrium contact angles of distilled water on materials following immersion in artificial saliva at 37±1°C at various time intervals, mean ± sd

Test period	Liquid (artificial saliva)				
	Vertex™Soft	EverSoft®	Molloplast-B®	Ufi Gel SC	BE
Initial	79.4 ± 3.1°	73.3 ± 4.5°	88.1 ± 3.9°	93.3 ± 3.6°	77.8 ± 3.9°
0.5 hour	78.7 ± 4.2°	77.4 ± 4.2°	87.9 ± 5.3°	89.8 ± 2.5°	79.3 ± 5.3°
1 hour	78.6 ± 5.7°	78.1 ± 3.7°	89.1 ± 4.3°	89.6 ± 4.8°	79.6 ± 3.7°
2 hours	81.6 ± 2.2°	78.6 ± 4.2°	89.0 ± 2.9°	88.1 ± 3.5°	78.8 ± 7.0°
4 hours	79.0 ± 4.3°	78.3 ± 3.7°	89.6 ± 4.3°	88.9 ± 2.5°	77.4 ± 3.9°
6 hours	79.9 ± 5.5°	78.0 ± 3.7°	86.3 ± 4.0°	88.4 ± 3.4°	78.6 ± 4.6°
1 day	79.3 ± 3.0°	76.6 ± 8.6°	86.6 ± 3.9°	88.1 ± 2.9°	78.8 ± 5.6°
2 days	81.2 ± 5.0°	76.3 ± 4.5°	86.6 ± 3.3°	89.0 ± 3.3°	78.0 ± 7.8°
3 days	81.3 ± 4.9°	77.7 ± 3.4°	87.5 ± 3.2°	88.6 ± 3.7°	77.3 ± 3.4°

1 week	79.6 ± 4.5°	75.3 ± 5.6°	87.5 ± 3.5°	86.5 ± 3.2°	77.6 ± 3.0°
2 weeks	83.3 ± 5.2°	77.9 ± 4.8°	88.8 ± 5.3°	87.5 ± 4.2°	77.2 ± 5.7°
3 weeks	79.9 ± 5.6°	78.7 ± 3.2°	87.2 ± 5.2°	89.8 ± 2.6°	75.9 ± 3.5°
1 month	82.8 ± 3.0°	77.6 ± 3.2°	87.1 ± 3.3°	87.9 ± 4.2°	76.0 ± 4.4°
2 months	78.4 ± 3.8°	77.1 ± 5.3°	88.5 ± 3.7°	88.2 ± 3.0°	76.9 ± 2.7°
4 months	80.9 ± 3.5°	77.4 ± 4.7°	87.9 ± 4.2°	90.2 ± 4.4°	76.9 ± 3.3°
6 months	79.2 ± 3.7°	76.1 ± 8.6°	87.8 ± 3.5°	89.2 ± 4.1°	75.7 ± 3.5°
1 year	77.4 ± 6.3°	74.3 ± 3.7°	87.1 ± 3.5°	89.0 ± 4.5°	76.6 ± 4.1°

Following immersion in artificial saliva at 37±1°C for one year, all materials showed little change in contact angle with time. The equilibrium contact angles between distilled water and MB and UG were significantly greater than on VT, ES and BE as processed and following immersion in artificial saliva.

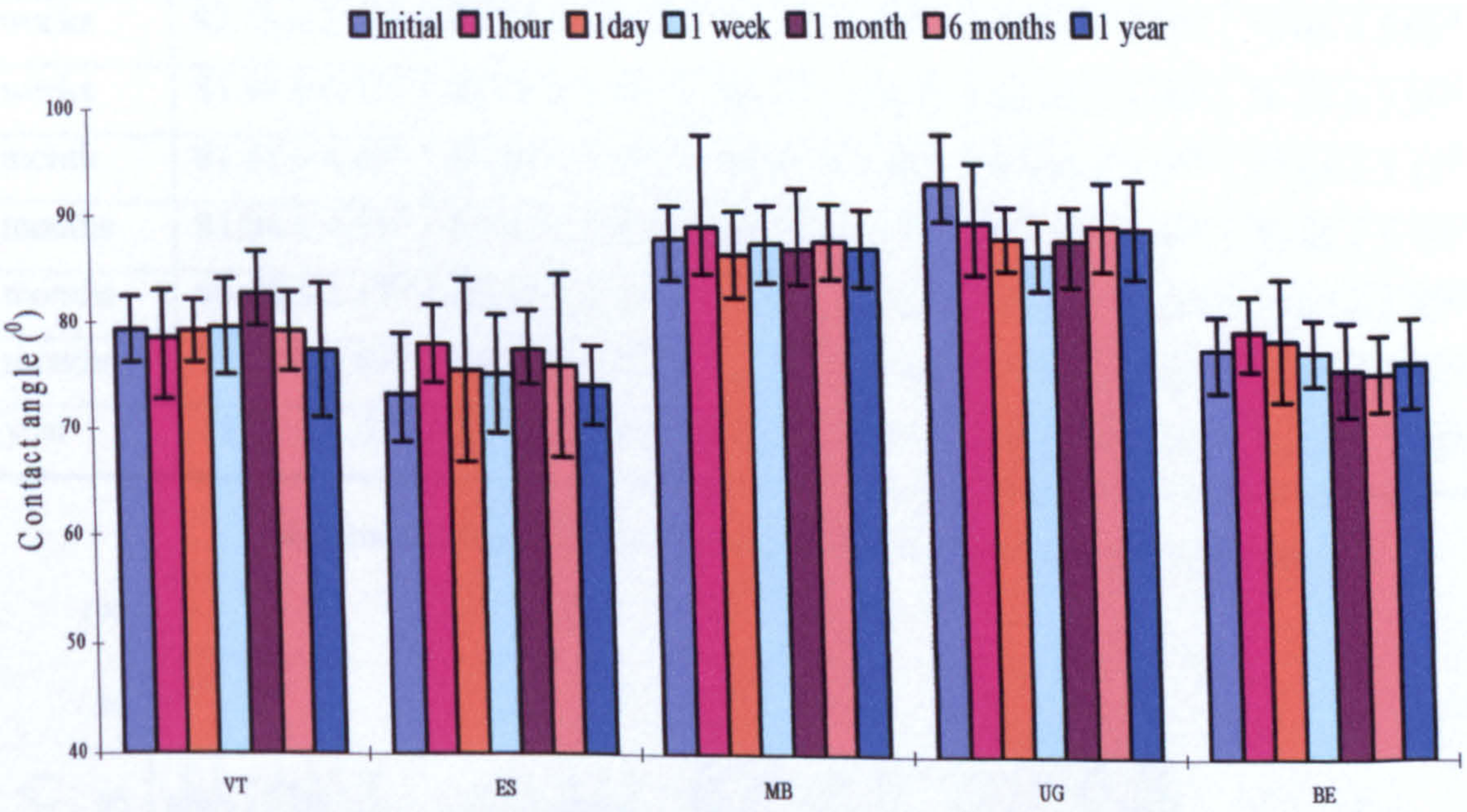


Figure 5.56 Equilibrium contact angles versus materials following immersion in artificial saliva.

5.4.3 Specimens stored in 3% acetic acid

Equilibrium contact angles of distilled water on denture soft lining materials as processed and following immersion in 3% acetic acid are given in Table 5.32. Figure 5.57 illustrates the wettability behaviour of materials following immersion.

Table 5.32 Summary of equilibrium contact angles of distilled water on materials following immersion in 3% acetic acid at 37±1°C at various time intervals, mean ± sd

Test period	Liquid (3% acetic acid)				
	Vertex™Soft	**EverSoft®**	**Molloplast-B®**	**Ufi Gel SC**	**BE**
Initial	80.71 ± 3.36°	74.29 ± 3.04°	88.37 ± 3.03°	90.33 ± 2.75°	76.11 ± 3.74°
0.5 hour	81.37 ± 3.32°	77.41 ± 4.91°	88.15 ± 5.75°	87.93 ± 3.36°	77.73 ± 3.53°
1 hour	80.55 ± 5.61°	77.86 ± 4.41°	87.19 ± 5.41°	89.10 ± 2.33°	77.65 ± 5.23°
2 hours	79.52 ± 4.32°	76.76 ± 4.51°	88.23 ± 3.04°	89.02 ± 3.53°	76.57 ± 3.10°
4 hours	79.87 ± 4.48°	77.59 ± 4.46°	88.76 ± 3.21°	87.72 ± 1.37°	79.91 ± 3.89°
6 hours	79.16 ± 3.23°	77.71 ± 4.58°	86.69 ± 3.73°	86.99 ± 3.60°	77.21 ± 4.24°
1 day	78.11 ± 4.57°	77.74 ± 5.16°	86.27 ± 3.61°	87.22 ± 2.56°	78.31 ± 8.24°
2 days	78.13 ± 4.57°	77.18 ± 3.63°	85.47 ± 3.13°	88.36 ± 3.50°	76.99 ± 6.24°
3 days	79.91 ± 3.39°	77.63 ± 5.71°	87.52 ± 2.92°	87.64 ± 3.97°	76.18 ± 5.45°
1 week	82.57 ± 6.24°	78.73 ± 5.02°	86.27 ± 4.38°	87.38 ± 4.93°	77.29 ± 3.47°
2 weeks	82.13 ± 2.56°	81.08 ± 6.99°	86.14 ± 3.10°	87.66 ± 4.29°	76.06 ± 5.05°
3 weeks	81.98 ± 6.12°	81.98 ± 1.93°	85.77 ± 3.93°	86.92 ± 2.09°	76.24 ± 2.89°
1 month	81.41 ± 4.05°	81.45 ± 5.78°	84.81 ± 1.70°	87.06 ± 3.89°	77.66 ± 5.15°
2 months	81.04 ± 4.51°	82.87 ± 3.60°	85.73 ± 1.58°	88.64 ± 3.90°	76.93 ± 5.75°
4 months	80.16 ± 4.17°	80.22 ± 4.33°	86.09 ± 1.75°	88.40 ± 3.18°	75.07 ± 1.47°
6 months	79.41 ± 4.87°	80.36 ± 4.36°	86.02 ± 2.44°	87.14 ± 1.86°	74.94 ± 4.02°
1 year	78.93 ± 4.62°	80.63 ± 3.68°	86.31 ± 2.82°	88.57 ± 3.18°	74.77 ± 3.45°

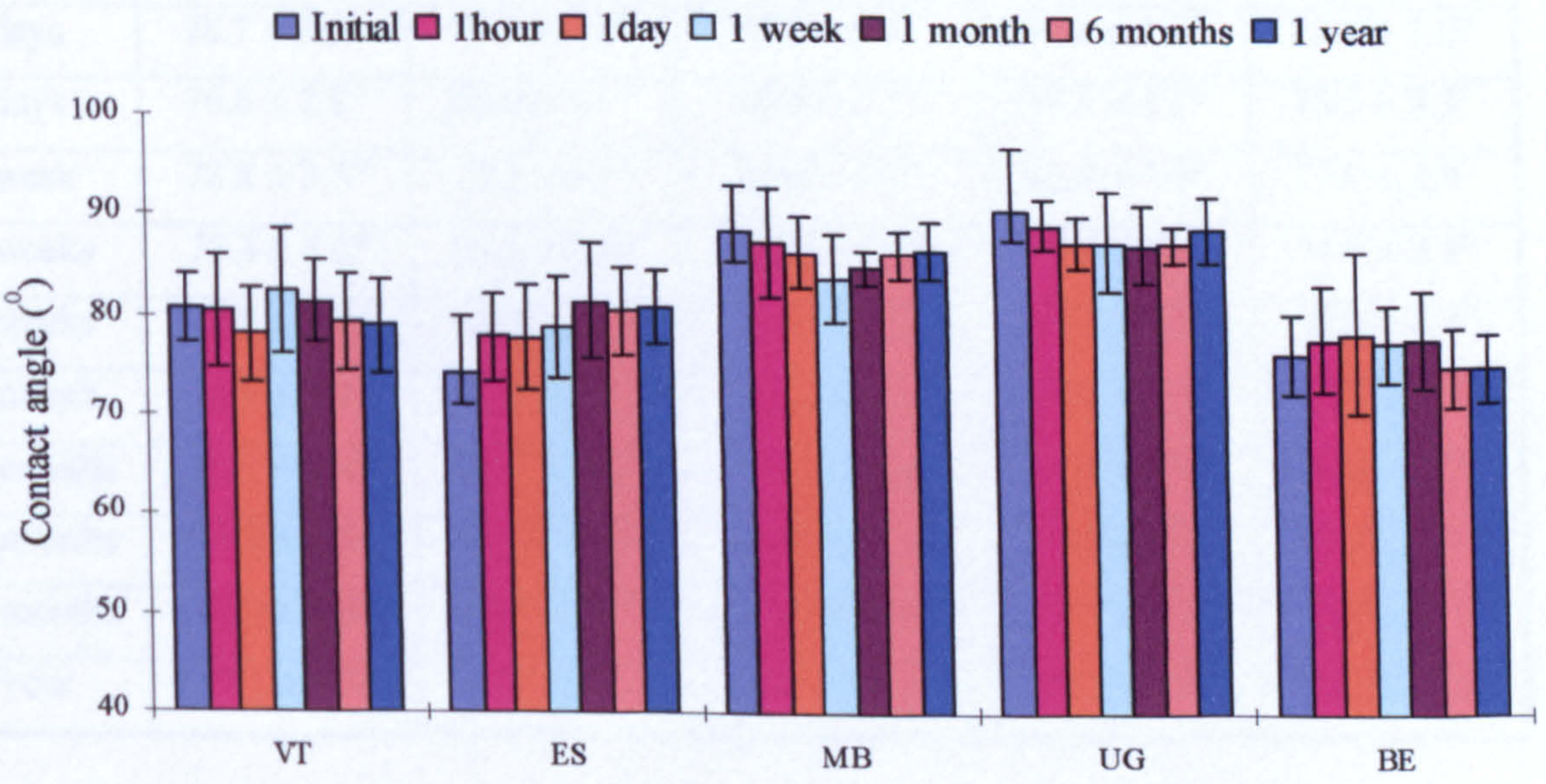


Figure 5.57 Equilibrium contact angles versus materials following immersion in 3% acetic acid.

Following immersion in 3% acetic acid at 37±1 °C for one year, all materials showed little change in contact angle with time. The equilibrium contact angles between distilled water and MB and UG were significantly greater than on VT, ES and BE as processed and following immersion in 3% acetic acid.

5.4.4 Specimens stored in 10% ethanol

Equilibrium contact angles of distilled water on denture soft lining materials as processed and following immersion in 10% ethanol are given in Table 5.33. Figure 5.58 illustrates the wettability behaviour of materials following immersion.

Table 5.33 Summary of equilibrium contact angles of distilled water on materials following immersion in 10% ethanol at 37±1°C at various time intervals, mean ± sd

Test period	Liquid (10% ethanol)				
	Vertex™Soft	EverSoft®	Molloplast-B®	Ufi Gel SC	BE
Initial	78.3 ± 4.1°	75.3 ± 4.6°	87.5 ± 2.0°	88.4 ± 6.6°	78.6 ± 4.4°
0.5 hour	79.3 ± 5.1°	77.6 ± 5.4°	85.7 ± 3.0°	88.5 ± 2.6°	79.5 ± 5.3°
1 hour	76.7 ± 5.6°	77.1 ± 3.2°	86.9 ± 1.7°	90.7 ± 4.2°	76.8 ± 4.7°
2 hours	80.0 ± 2.5°	74.7 ± 4.4°	86.8 ± 2.6°	90.6 ± 3.9°	76.4 ± 4.9°
4 hours	79.3 ± 5.3°	77.7 ± 4.6°	86.1 ± 2.6°	89.4 ± 3.3°	71.9 ± 3.7°
6 hours	80.1 ± 4.9°	77.8 ± 4.8°	86.9 ± 2.7°	87.9 ± 3.1°	71.7 ± 4.8°
1 day	77.8 ± 4.4°	77.7 ± 3.4°	84.5 ± 3.6°	87.4 ± 3.4°	72.1 ± 2.9°
2 days	78.7 ± 3.9°	79.2 ± 4.4°	84.0 ± 2.8°	89.4 ± 2.8°	73.1 ± 3.0°
3 days	76.6 ± 2.8°	80.0 ± 3.5°	82.4 ± 3.7°	87.5 ± 4.2°	75.5 ± 3.3°
1 week	78.8 ± 3.3°	79.2 ± 3.8°	81.4 ± 3.9°	88.4 ± 4.9°	75.0 ± 2.9°
2 weeks	77.3 ± 5.6°	82.1 ± 3.5°	84.3 ± 2.5°	89.2 ± 4.6°	74.9 ± 3.8°
3 weeks	78.8 ± 5.4°	81.9 ± 4.0°	86.1 ± 3.7°	90.0 ± 3.8°	75.4 ± 4.4°
1 month	78.9 ± 5.7°	82.0 ± 4.6°	83.4 ± 5.5°	88.1 ± 4.5°	75.7 ± 5.3°
2 months	79.1 ± 3.4°	78.3 ± 3.9°	84.1 ± 4.4°	88.3 ± 3.9°	74.8 ± 1.7°
4 months	78.8 ± 3.5°	80.6 ± 5.0°	84.9 ± 4.4°	90.9 ± 5.2°	74.4 ± 3.9°
6 months	78.9 ± 5.5°	80.9 ± 3.7°	83.8 ± 5.3°	87.3 ± 2.9°	75.0 ± 5.1°
1 year	77.1 ± 5.3°	80.3 ± 4.9°	84.6 ± 3.5°	88.1 ± 4.4°	74.4 ± 4.4°

Following immersion in 10% ethanol at 37±1°C for one year, all materials showed little change in contact angle with time. The equilibrium contact angles between distilled water and MB and UG were significantly greater than on VT, ES and BE as processed and following immersion in 10% ethanol.

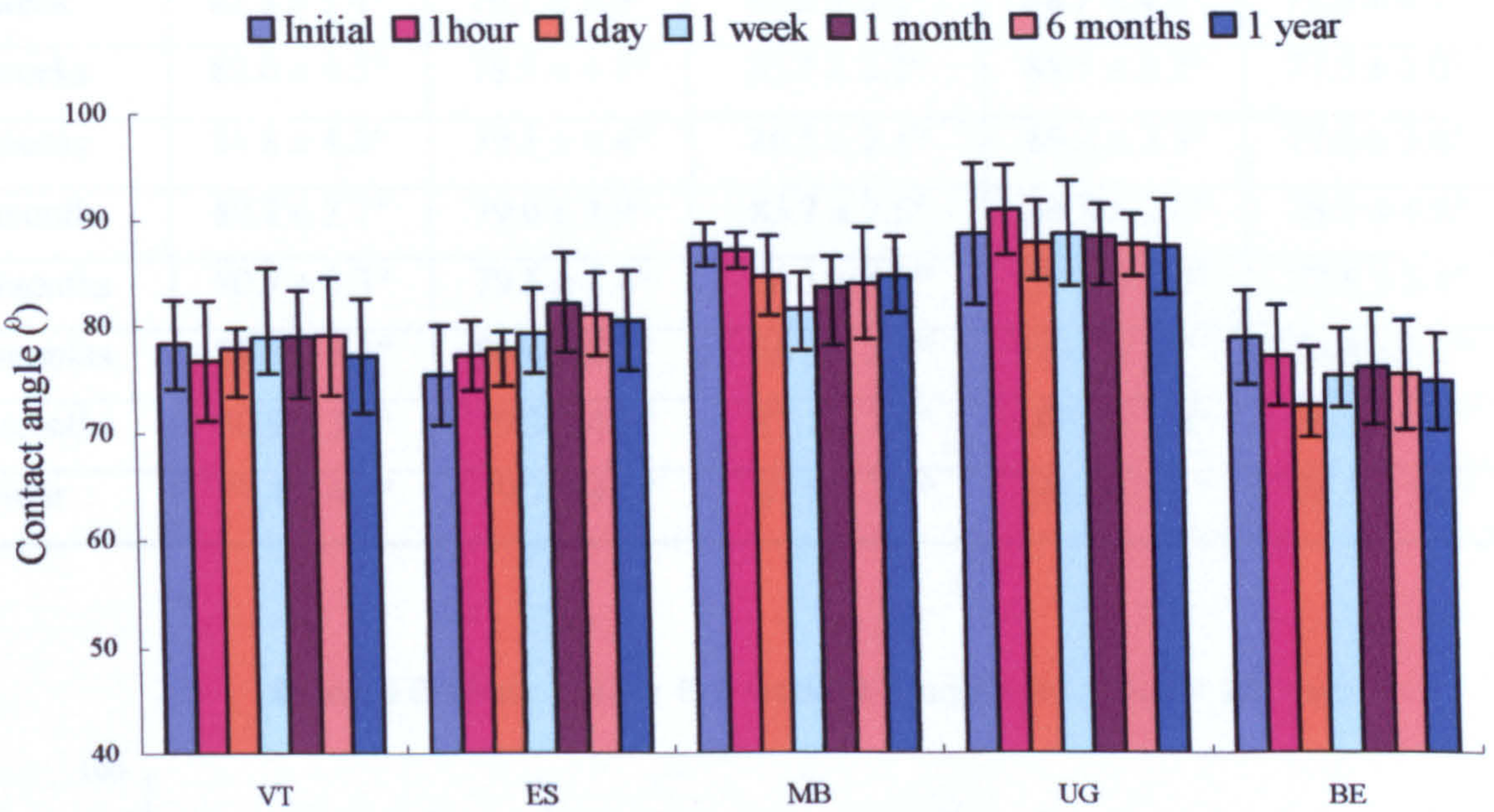


Figure 5.58 Equilibrium contact angles versus materials following immersion in 10% ethanol.

5.4.5 Specimens stored in 50% ethanol

Equilibrium contact angles of distilled water on denture soft lining materials as processed and following immersion in 50% ethanol are given in Table 5.34. Figure 5.59 illustrates the wettability behaviour of materials following immersion.

Table 5.34 Summary of equilibrium contact angles of distilled water on materials following immersion in 50% ethanol 37±1°C at various time intervals, mean ± sd

Test period	Liquid (50% ethanol)				
	Vertex™Soft	EverSoft®	Molloplast-B®	Ufi Gel SC	BE
Initial	78.9 ± 4.2°	76.8 ± 3.1°	87.0 ± 3.6°	89.8 ± 2.6°	79.1 ± 3.9°
0.5 hour	80.4 ± 4.6°	79.1 ± 3.1°	86.8 ± 5.7°	90.4 ± 2.9°	81.2 ± 4.7°
1 hour	80.9 ± 6.0°	79.0 ± 3.1°	86.2 ± 3.4°	89.3 ± 2.5°	78.8 ± 5.5°
2 hours	80.9 ± 2.6°	78.9 ± 3.7°	87.9 ± 3.4°	89.8 ± 1.9°	78.3 ± 3.5°

4 hours	81.5 ± 4.6°	79.1 ± 3.3°	87.7 ± 2.5°	89.7 ± 3.1°	79.1 ± 2.0°
6 hours	81.4 ± 4.2°	78.9 ± 3.5°	87.7 ± 5.5°	88.9 ± 2.6°	77.4 ± 5.1°
1 day	81.1 ± 4.3°	77.9 ± 2.0°	85.1 ± 3.5°	87.3 ± 3.2°	77.6 ± 4.4°
2 days	82.8 ± 4.1°	76.4 ± 5.2°	85.6 ± 2.7°	87.9 ± 3.1°	78.5 ± 4.0°
3 days	83.0 ± 3.8°	79.2 ± 3.8°	86.2 ± 3.2°	88.5 ± 3.9°	77.7 ± 4.3°
1 week	82.3 ± 3.4°	79.7 ± 3.6°	85.6 ± 3.1°	88.7 ± 4.0°	77.0 ± 4.1°
2 weeks	82.0 ± 4.5°	78.5 ± 4.7°	85.1 ± 3.2°	88.1 ± 3.2°	77.5 ± 3.0°
3 weeks	81.8 ± 4.8°	79.3 ± 4.4°	86.5 ± 3.1°	89.2 ± 3.3°	77.6 ± 3.6°
1 month	80.8 ± 2.7°	79.0 ± 4.9°	85.7 ± 2.6°	88.8 ± 2.6°	78.1 ± 4.8°
2 months	80.7 ± 3.3°	79.5 ± 3.6°	86.1 ± 4.2°	88.4 ± 4.0°	77.8 ± 3.4°
4 months	81.2 ± 3.1°	80.4 ± 2.8°	86.5 ± 2.9°	90.7 ± 4.7°	76.8 ± 5.1°
6 months	80.9 ± 3.1°	79.3 ± 4.5°	87.1 ± 2.2°	87.5 ± 3.4°	76.5 ± 2.8°
1 year	79.4 ± 4.7°	79.7 ± 4.4°	87.5 ± 3.1°	88.6 ± 3.1°	76.3 ± 3.6°

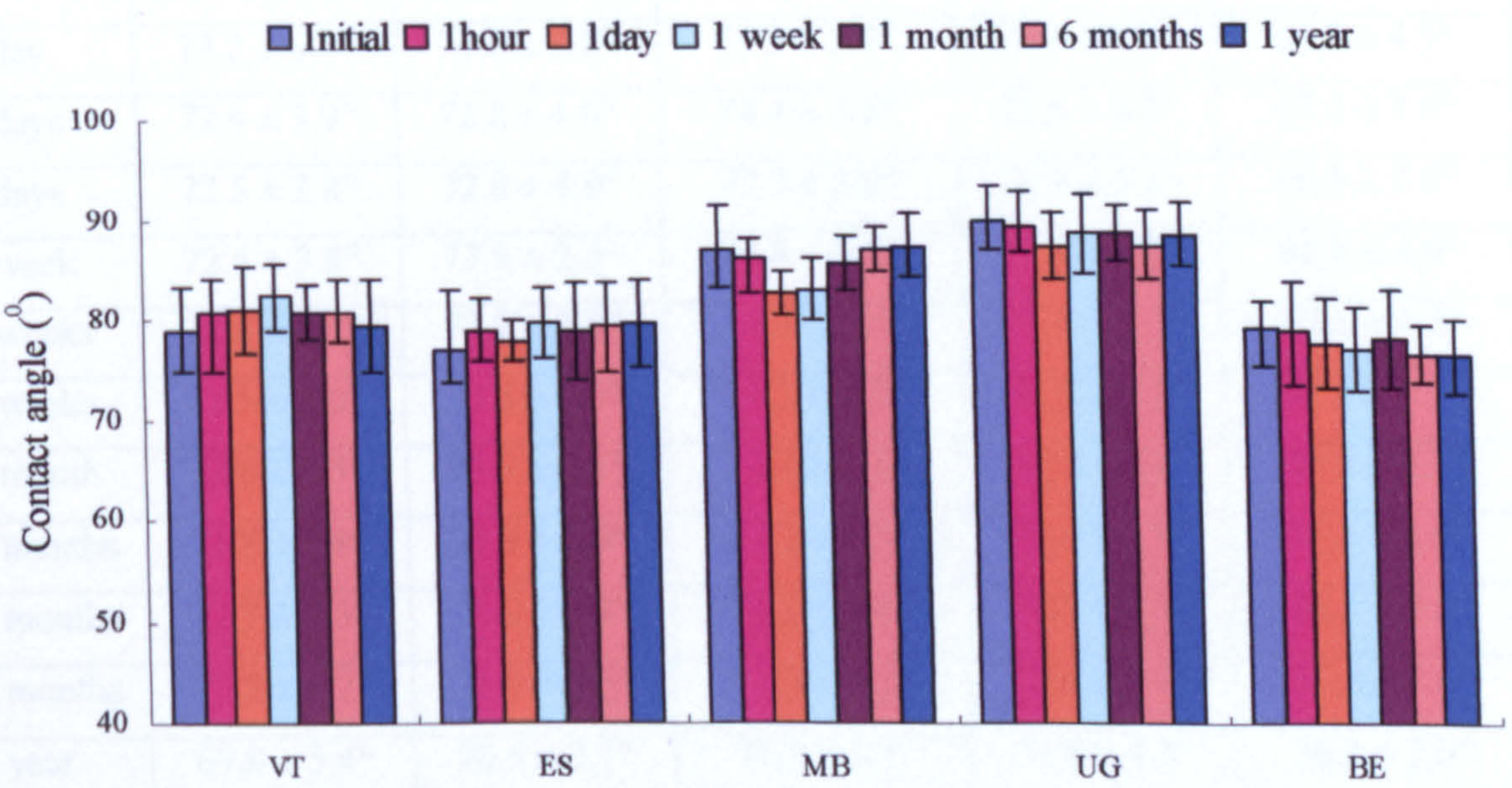


Figure 5.59 Equilibrium contact angles versus materials following immersion in 50% ethanol.

Following immersion in 50% ethanol at 37±1°C for one year, all materials showed little change in contact angle with time. The equilibrium contact angles between distilled water and MB and UG were significantly greater than on VT, ES and BE as processed and following immersion in 50% ethanol.

5.4.6 Specimens stored in coconut oil

Equilibrium contact angles of distilled water on denture soft lining materials as processed and following immersion in coconut oil are given in Table 5.35. Figure 5.60 illustrates the wettability behaviour of materials following immersion.

Table 5.35 Summary of equilibrium contact angles of distilled water on materials following immersion in coconut oil at 37±1°C at various time intervals, mean ± sd

Test period	Liquid (coconut oil)				
	Vertex™Soft	EverSoft®	Molloplast-B®	Ufi Gel SC	BE
Initial	80.7 ± 4.3°	74.3 ± 3.3°	87.0 ± 1.8°	91.0 ± 2.8°	79.2 ± 3.5°
0.5 hour	75.5 ± 3.0°	74.4 ± 4.8°	80.8 ± 3.2°	89.4 ± 2.3°	71.2 ± 6.8°
1 hour	76.0 ± 6.6°	72.9 ± 2.9°	79.7 ± 4.9°	85.3 ± 5.2°	67.0 ± 7.5°
2 hours	77.9 ± 6.0°	74.8 ± 4.1°	79.4 ± 5.4°	86.8 ± 3.5°	67.4 ± 5.7°
4 hours	73.0 ± 4.3°	73.2 ± 3.5°	79.3 ± 2.7°	85.2 ± 2.8°	63.2 ± 5.3°
6 hours	74.0 ± 6.2°	73.0 ± 2.3°	78.4 ± 4.2°	79.4 ± 3.1°	65.7 ± 6.1°
1 day	73.2 ± 6.3°	74.0 ± 3.8°	75.5 ± 3.2°	75.6 ± 3.2°	64.7 ± 4.5°
2 days	72.4 ± 3.9°	72.8 ± 4.6°	74.4 ± 5.8°	75.5 ± 8.2°	67.4 ± 4.0°
3 days	72.5 ± 3.8°	72.8 ± 4.9°	77.3 ± 3.0°	76.9 ± 5.2°	66.6 ± 3.9°
1 week	72.6 ± 3.8°	73.9 ± 2.5°	74.8 ± 3.5°	77.0 ± 5.3°	66.8 ± 4.9°
2 weeks	71.6 ± 6.1°	73.7 ± 2.0°	74.3 ± 2.6°	75.4 ± 4.2°	67.6 ± 4.2°
3 weeks	71.5 ± 6.0°	73.8 ± 3.9°	74.3 ± 5.5°	75.8 ± 4.7°	63.8 ± 4.5°
1 month	72.6 ± 4.5°	73.9 ± 4.1°	74.4 ± 4.4°	75.0 ± 4.8°	59.5 ± 2.7°
2 months	71.8 ± 4.8°	73.9 ± 3.9°	75.3 ± 5.6°	76.6 ± 3.8°	55.4 ± 2.6°
4 months	72.3 ± 3.3°	71.8 ± 2.4°	76.0 ± 3.4°	76.4 ± 5.5°	56.2 ± 3.5°
6 months	70.5 ± 6.2°	71.4 ± 4.5°	72.8 ± 6.1°	72.6 ± 5.8°	56.2 ± 3.6°
1 year	69.8 ± 5.4°	70.5 ± 3.7°	71.5 ± 5.1°	71.0 ± 4.8°	56.2 ± 2.9°

Following immersion in coconut oil at 37±1°C for one year, all materials showed a decrease in equilibrium contact angle with time with the exception of ES which showed little change.

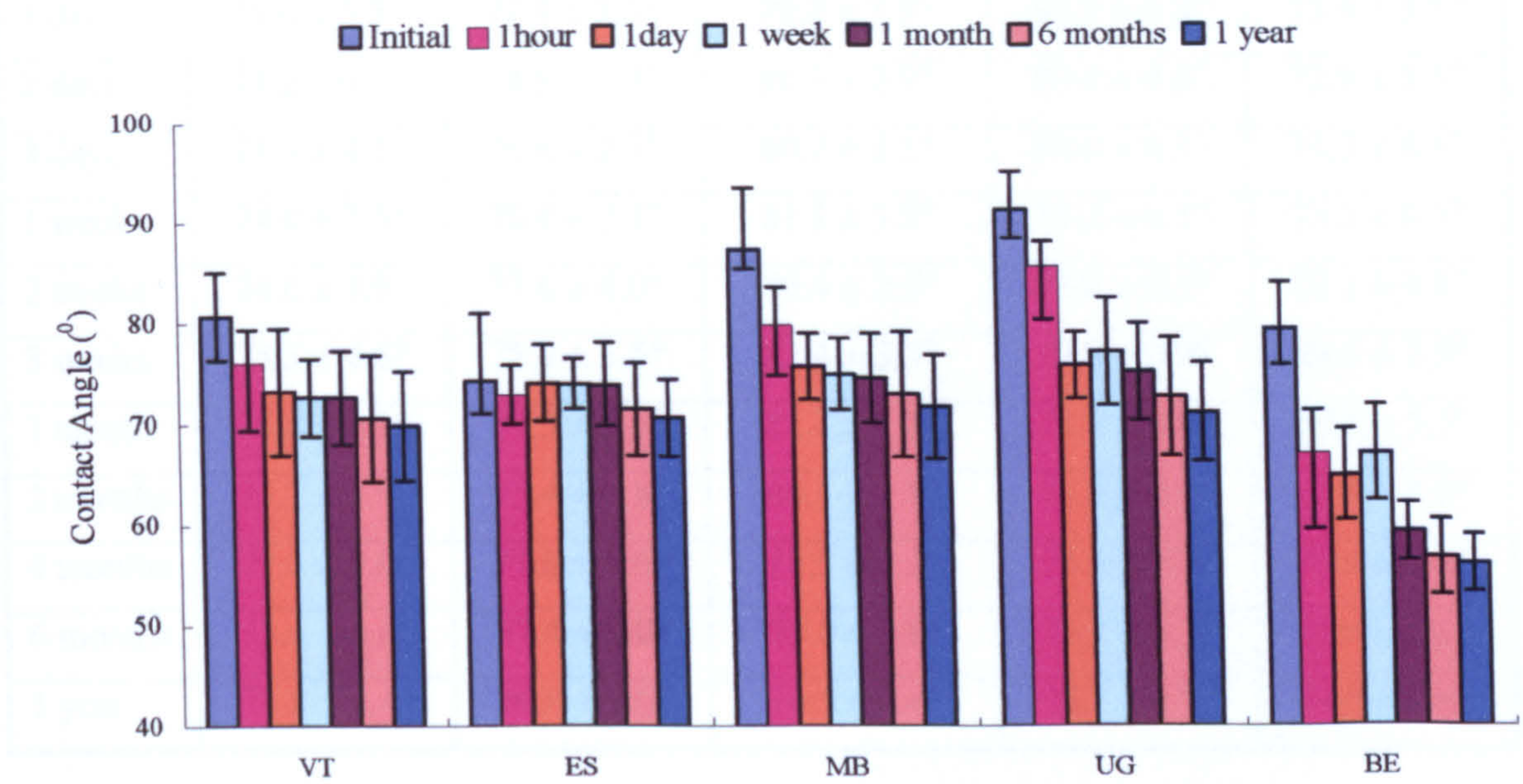


Figure 5.60 Equilibrium contact angles versus materials following immersion in coconut oil.

5.4.7 Specimens stored in HB307

Equilibrium contact angles of distilled water on denture soft lining materials as processed and following immersion in HB307 are given in Table 5.36. Figure 5.61 illustrates the wettability behaviour of materials following immersion.

Following immersion in HB307 at 37±1°C for one year, all materials showed a decrease in equilibrium contact angle with time with the exception of ES which showed little change.

Table 5.36 Summary of equilibrium contact angles of distilled water on materials following immersion in HB307 at 37±1°C at various time intervals, mean ± sd

Test period	Liquid (HB307)				
	Vertex™Soft	EverSoft®	Molloplast-B®	Ufi Gel SC	BE
Initial	79.3 ± 4.2°	74.3 ± 2.4°	86.1 ± 3.0°	87.9 ± 2.9°	80.2 ± 3.3°
0.5 hour	77.4 ± 3.4°	74.2 ± 3.5°	83.9 ± 3.6°	90.5 ± 2.2°	80.9 ± 3.4°
1 hour	78.3 ± 5.4°	74.6 ± 3.6°	81.5 ± 2.7°	91.1 ± 3.1°	77.0 ± 3.7°
2 hours	75.8 ± 3.6°	75.5 ± 4.5°	82.2 ± 2.2°	90.7 ± 2.7°	75.5 ± 3.9°
4 hours	77.7 ± 6.2°	76.3 ± 3.3°	80.6 ± 2.4°	89.8 ± 2.3°	77.9 ± 3.3°
6 hours	77.1 ± 6.7°	74.0 ± 3.6°	80.9 ± 3.7°	88.1 ± 2.0°	74.4 ± 8.0°

1 day	75.6 ± 5.3°	77.3 ± 2.5°	79.2 ± 3.8°	86.5 ± 6.0°	75.4 ± 3.5°
2 days	74.2 ± 6.7°	74.5 ± 2.3°	80.5 ± 2.9°	80.4 ± 4.6°	72.9 ± 5.5°
3 days	74.5 ± 4.1°	76.6 ± 2.7°	80.7 ± 2.5°	80.0 ± 6.1°	71.7 ± 6.5°
1 week	74.0 ± 2.5°	76.4 ± 2.7°	81.1 ± 3.8°	77.2 ± 6.1°	73.2 ± 6.1°
2 weeks	74.6 ± 3.9°	77.6 ± 4.0°	80.4 ± 2.0°	78.8 ± 6.5°	72.1 ± 4.8°
3 weeks	78.5 ± 4.6°	75.3 ± 3.5°	82.4 ± 3.3°	77.9 ± 3.9°	68.4 ± 7.5°
1 month	74.4 ± 5.1°	77.3 ± 7.5°	82.7 ± 7.1°	78.1 ± 4.1°	69.2 ± 5.5°
2 months	75.7 ± 3.9°	75.4 ± 5.8°	80.5 ± 2.8°	78.0 ± 4.1°	67.8 ± 4.0°
4 months	77.3 ± 2.0°	77.8 ± 3.6°	78.5 ± 5.1°	76.2 ± 4.3°	Not tested
6 months	73.6 ± 4.0°	77.4 ± 3.0°	76.8 ± 2.6°	76.2 ± 5.7°	Not tested
1 year	73.8 ± 3.4°	76.8 ± 3.9°	76.5 ± 3.6°	76.2 ± 3.9°	Not tested

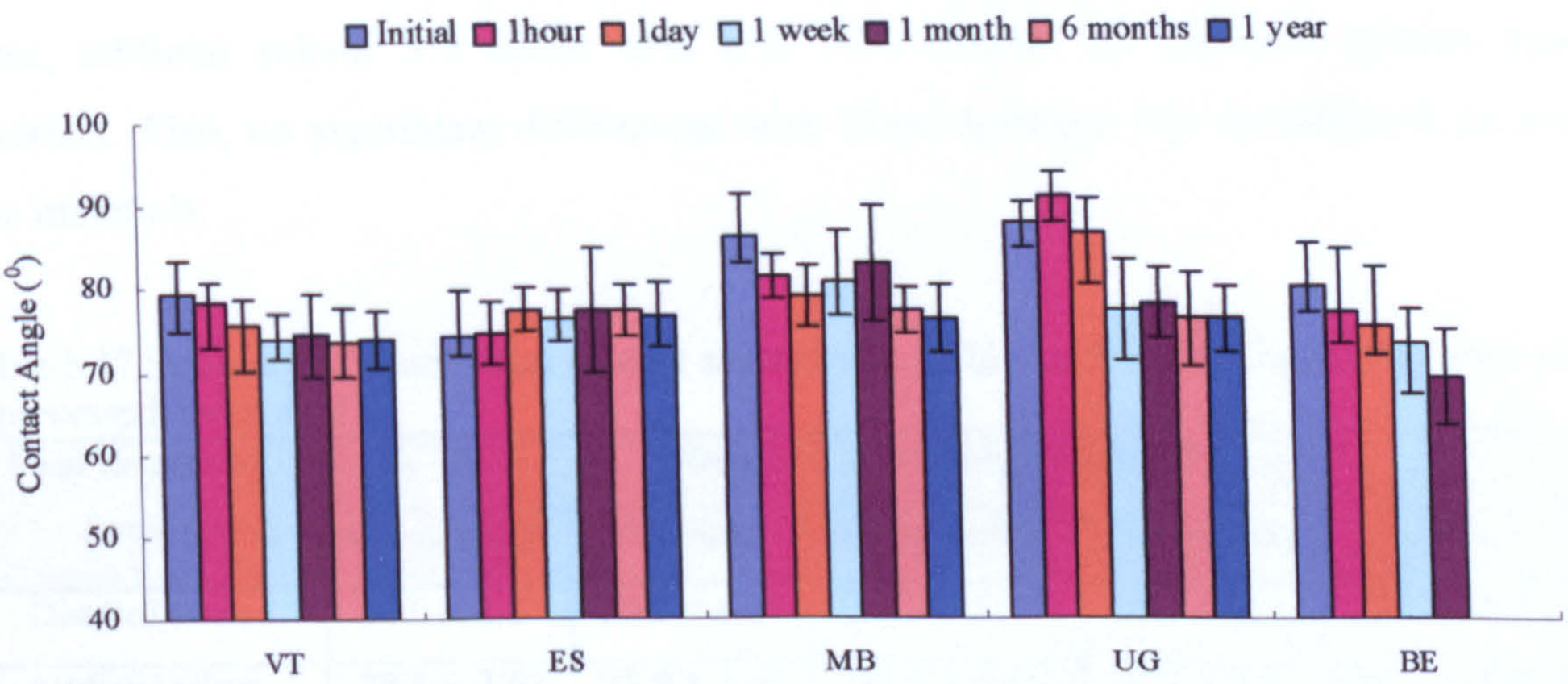


Figure 5.61 Equilibrium contact angles versus materials following immersion in HB307.

5.4.8 Equilibrium contact angle between various food simulating liquids and the denture soft lining materials at various time intervals

The equilibrium contact angle measurements between various food simulating liquids and the denture soft lining materials as processed, and after immersion in the same food simulating liquids for one day, one week, one month and one year are presented in Tables 5.37-41. Table 5.37 demonstrates that oils on VT and ES had the lowest equilibrium

contact angle value, and artificial saliva on MB and UG had the largest equilibrium contact angle. 3% acetic acid and 10% ethanol on specimens gave similar results.

Tables 5.38-41 demonstrate that oils on VT and ES following immersion at one day, one week, one month and one year, respectively, had the lowest equilibrium angle values in oils. MB, UG and BE following immersion at one day, one week, one month and one year, respectively, also had lower equilibrium contact angles in oils than in other food simulating liquids.

The differences among the food simulating liquids and materials were significant ($P<0.01$). Analysis of the data revealed that significant differences were found between food simulating liquids and materials. There were no differences found between distilled water, artificial saliva, 3% acetic acid and 10% ethanol on different generic type materials. Also, no significant differences were found between oils on different generic type materials.

Table 5.37 Summary of equilibrium contact angles between food simulating liquids and materials as processed, mean ± sd

Food simulating liquids	Denture soft lining materials				
	Vertex™Soft	EverSoft®	Molloplast-B®	Ufi Gel SC	BE
Distilled water	84.0 ± 2.5°	73.0 ± 4.5°	89.5 ± 4.2°	90.7 ± 2.9°	78.6 ± 4.4°
Artificial saliva	78.6 ± 3.5°	75.9 ± 3.9°	92.8 ± 3.6°	92.7 ± 4.6°	80.1 ± 4.4°
3% acetic acid	75.9 ± 3.4°	75.0 ± 1.9°	79.4 ± 2.6°	88.7 ± 3.2°	79.5 ± 6.9°
10% ethanol	78.4 ± 2.9°	77.1 ± 3.0°	80.9 ± 3.5°	90.3 ± 5.6°	80.8 ± 4.3°
50% ethanol	52.6 ± 4.3°	46.2 ± 7.1°	62.1 ± 6.8°	65.8 ± 2.7°	50.1 ± 6.6°
Coconut oil	15.2 ± 3.5°	20.9 ± 2.6°	63.9 ± 1.4°	57.2 ± 2.8°	49.2 ± 5.9°
HB307	10.1 ± 2.8°	14.6 ± 5.4°	56.4 ± 3.0°	53.9 ± 3.4°	44.8 ± 6.4°

Table 5.38 Summary of equilibrium contact angles between food simulating liquids and materials following one day immersion, mean ± sd

Food simulating liquids	Denture soft lining materials				
	Vertex™Soft	EverSoft®	Molloplast-B®	Ufi Gel SC	BE
Distilled water	80.9 ± 4.0°	73.1 ± 2.8°	90.0 ± 3.4°	87.7 ± 5.6°	73.3 ± 3.0°
Artificial saliva	76.1 ± 4.5°	74.4 ± 7.1°	85.3 ± 4.5°	80.9 ± 4.8°	85.1 ± 3.3°
3% acetic acid	76.2 ± 4.1°	73.9 ± 1.4°	80.4 ± 3.6°	87.9 ± 1.5°	82.8 ± 4.8°
10% ethanol	76.7 ± 4.8°	77.2 ± 3.0°	83.3 ± 8.1°	85.6 ± 5.3°	74.9 ± 4.3°
50% ethanol	52.6 ± 5.1°	54.3 ± 2.2°	65.1 ± 3.6°	61.5 ± 4.2°	49.5 ± 4.7°
Coconut oil	28.4 ± 4.7°	13.6 ± 6.1°	57.5 ± 6.9°	54.2 ± 6.9°	24.3 ± 4.3°
HB307	16.7 ± 1.4°	29.2 ± 4.7°	57.9 ± 3.2°	52.7 ± 4.9°	47.5 ± 2.1°

Table 5.39 Summary of equilibrium contact angles between food simulating liquids and materials following one week immersion, mean ± sd

Food simulating liquids	Denture soft lining materials				
	Vertex™Soft	EverSoft®	Molloplast-B®	Ufi Gel SC	BE
Distilled water	83.3 ± 1.4°	75.4 ± 1.4°	86.5 ± 2.4°	87.9 ± 2.5°	74.5 ± 5.7°
Artificial saliva	77.2 ± 3.9°	76.9 ± 3.2°	87.9 ± 2.5°	78.6 ± 6.8°	85.0 ± 1.8°
3% acetic acid	80.0 ± 2.1°	76.0 ± 3.3°	81.6 ± 3.6°	82.3 ± 4.5°	79.3 ± 2.2°
10% ethanol	76.0 ± 4.1°	80.0 ± 2.7°	86.9 ± 2.1°	82.8 ± 2.6°	81.1 ± 1.7°
50% ethanol	52.9 ± 4.1°	51.9 ± 7.1°	65.9 ± 4.2°	60.5 ± 5.2°	53.3 ± 2.4°
Coconut oil	23.1 ± 2.1°	14.2 ± 2.6°	59.9 ± 3.7°	55.4 ± 7.5°	24.8 ± 6.8°
HB307	23.5 ± 6.7°	25.0 ± 1.6°	58.1 ± 4.7°	57.8 ± 4.1°	45.8 ± 3.7°

Table 5.40 Summary of equilibrium contact angles between food simulating liquids and materials following one month immersion, mean ± sd

Food simulating liquids	Denture soft lining materials				
	Vertex™Soft	EverSoft®	Molloplast-B®	Ufi Gel SC	BE
Distilled water	80.4 ± 5.2°	78.5 ± 5.4°	87.3 ± 2.8°	88.9 ± 5.3°	75.7 ± 5.3°
Artificial saliva	79.5 ± 8.4°	84.0 ± 2.5°	90.4 ± 5.2°	83.3 ± 3.4°	83.9 ± 3.9°
3% acetic acid	80.4 ± 3.9°	78.1 ± 0.4°	82.8 ± 2.4°	86.7 ± 2.8°	80.6 ± 6.9°
10% ethanol	78.1 ± 0.9°	80.9 ± 1.3°	84.8 ± 2.1°	82.5 ± 4.2°	80.9 ± 1.6°
50% ethanol	52.4 ± 3.2°	50.6 ± 4.8°	66.1 ± 2.2°	58.9 ± 4.0°	54.1 ± 8.0°
Coconut oil	22.6 ± 1.4°	15.1 ± 2.3°	58.6 ± 4.1°	59.5 ± 3.3°	13.4 ± 2.3°
HB307	22.2 ± 2.7°	15.5 ± 1.1°	52.6 ± 3.7°	55.6 ± 4.9°	14.0 ± 2.6°

Table 5.41 Summary of equilibrium contact angles between food simulating liquids and materials following one year immersion, mean ± sd

Food simulating liquids	Denture soft lining materials				
	Vertex™Soft	EverSoft®	Molloplast-B®	Ufi Gel SC	BE
Distilled water	77.8 ± 4.6°	79.8 ± 3.4°	88.2 ± 2.6°	88.2 ± 5.4°	73.7 ± 4.6°
Artificial saliva	75.2 ± 3.0°	82.5 ± 1.2°	89.4 ± 3.1°	89.1± 3.1°	81.8 ± 1.9°
3% acetic acid	79.0 ± 3.5°	82.5 ± 3.8°	81.3 ± 5.6°	90.2 ± 2.1°	76.2 ± 4.8°
10% ethanol	77.1 ± 3.3°	77.5 ± 6.2°	86.9 ± 5.6°	84.3 ± 2.4°	76.9 ± 6.0°
50% ethanol	59.7 ± 2.9°	57.0 ± 4.6°	63.4 ± 4.0°	66.2 ± 2.1°	55.5 ± 5.4°
Coconut oil	14.4 ± 7.4°	13.6 ± 6.0°	53.7 ± 9.2°	51.3 ± 3.0°	11.2 ± 3.2°
HB307	24.6 ± 5.2°	22.0 ± 3.0°	56.8 ± 4.8°	56.9 ± 5.7°	Not tested

5.5 Particle Size Analysis

Table 5.42 and Figure 5.62 show the average polyethyl methacrylate particle size of Vertex™Soft and EverSoft®, and their particle distributions.

Table 5.42 Particle size of commercial polymer powders.

Material powder	Average Particle Size, μm D[*v*,0.5]	Sd
Vertex™Soft	62.7	0.6
EverSoft®	44.0	0.6

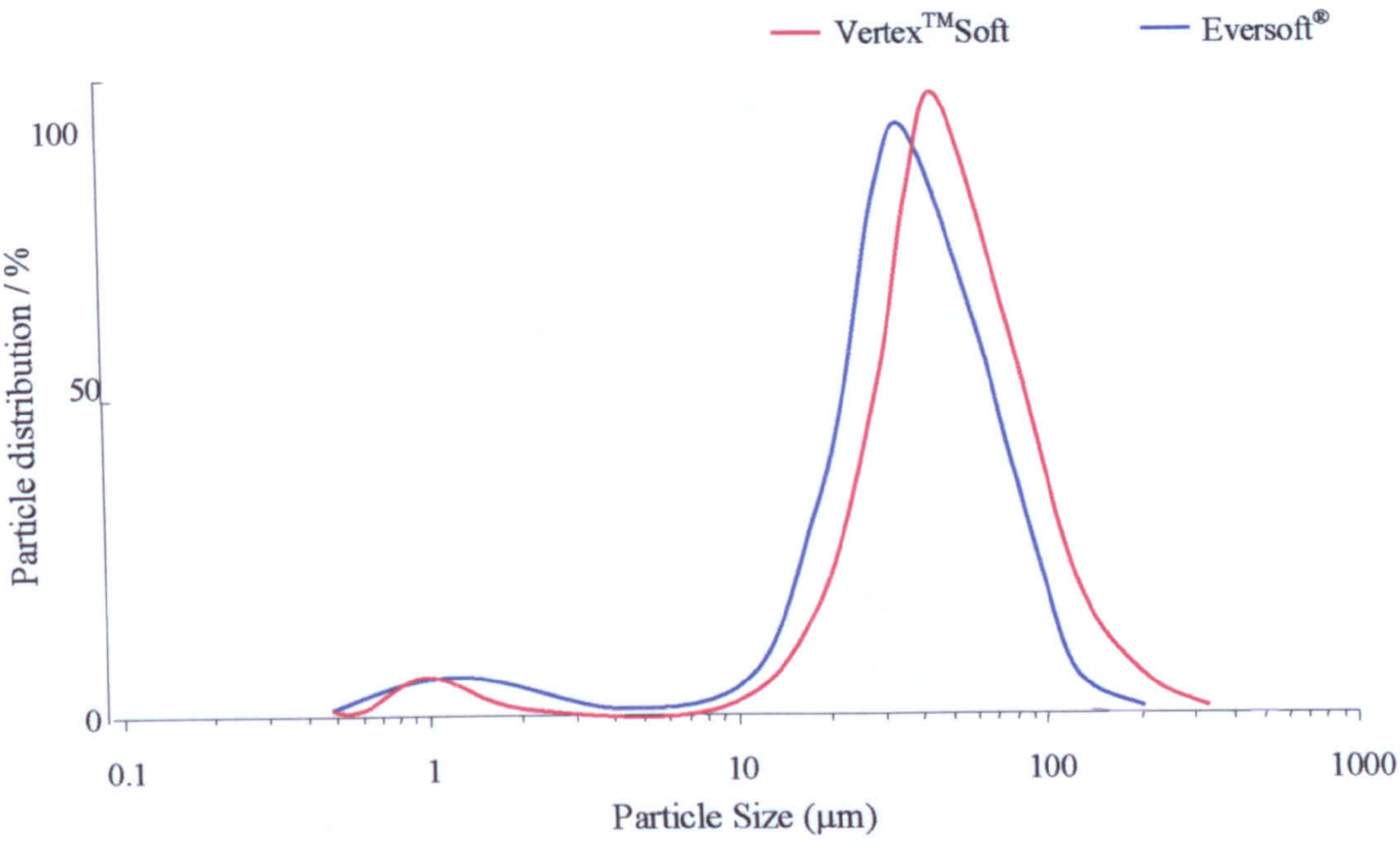


Figure 5.62 Particle distributions of Vertex™Soft and EverSoft® polymer powders.

Vertex™Soft and EverSoft® polyethyl methacrylate polymer particles ranged in size from approximately 0.5 μm to 600.0 μm, and with peaks at 60.0 μm and 45.0 μm, respectively. The bulk distribution of particle size was relatively symmetrical.

5.6 Leachable substance graph

Representative spectra of immersion fluids recorded after storage of Vertex™Soft, EverSoft®, Molloplast-B®, Ufi-Gel SC and bromo-butyl butyl elastomer for a prolonged period are given in Figs 5.63-69. The FTIR spectra of the immersion fluids from the four commercial denture soft lining materials (Vertex™Soft, EverSoft®, Molloplast-B®, Ufi-Gel SC) and bromo-butyl butyl elastomer were similar in appearance for one year storage. Plots are independently offset for absorbance to facilitate comparison. No leachable substances were found in these immersion fluids after one year of denture soft lining materials storage. There was virtually no shift in absorption band position between control and sample solutions.

The spectrum for water shows characteristics bands at 3270 and 1633 cm^{-1}, both of which are quite broad. In ethanol/water liquids, the ethanol carbonyl peak is at 1043 cm^{-1}. There

is no sign of peaks at 1600 cm^{-1} (aromatic-phthalates have a doublet), 1730 cm^{-1} (carbonyl ester peak), and the 1280 cm^{-1} attributable to phthalates. This means that the level of phthalate in the distilled water is below the resolvable level.

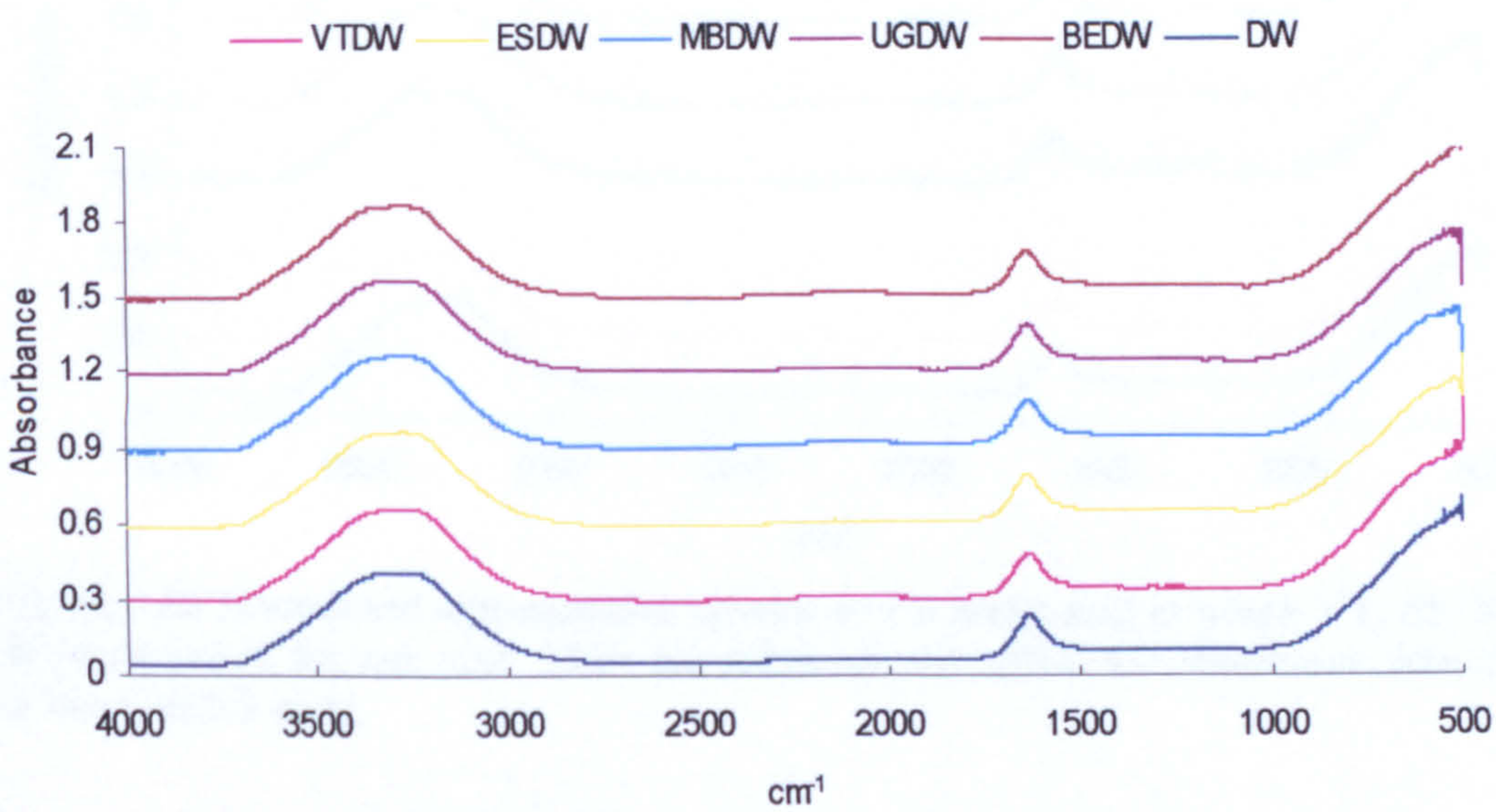


Figure 5.63 Normalized representative spectra of distilled water in which VT, ES, MB, UG and BE were stored for one year. Plots are independently offset for absorbance (absorbance scale division are 0.3 unit).

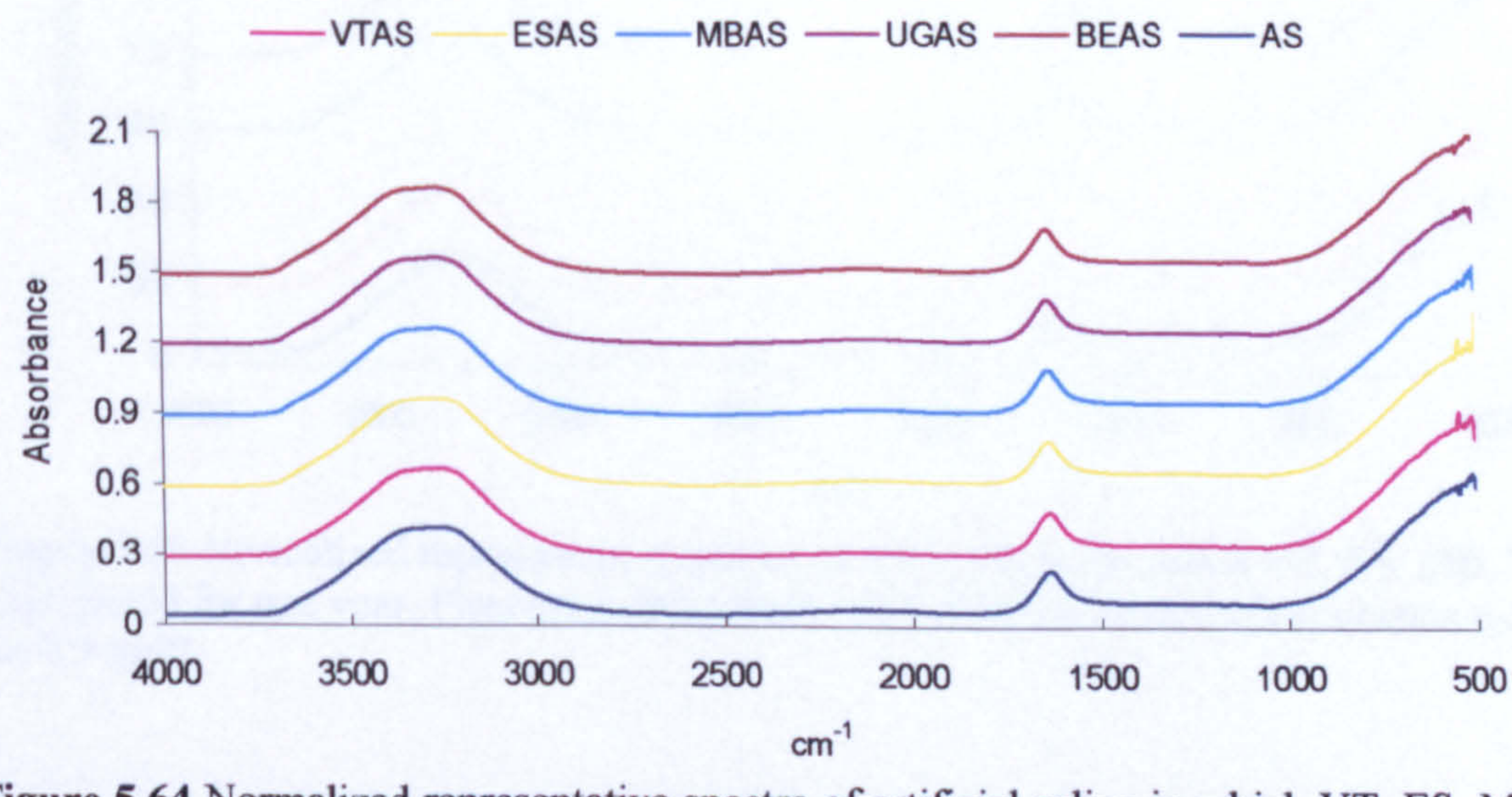


Figure 5.64 Normalized representative spectra of artificial saliva in which VT, ES, MB, UG and BE were stored for one year. Plots are independently offset for absorbance (absorbance scale division are 0.3 unit).

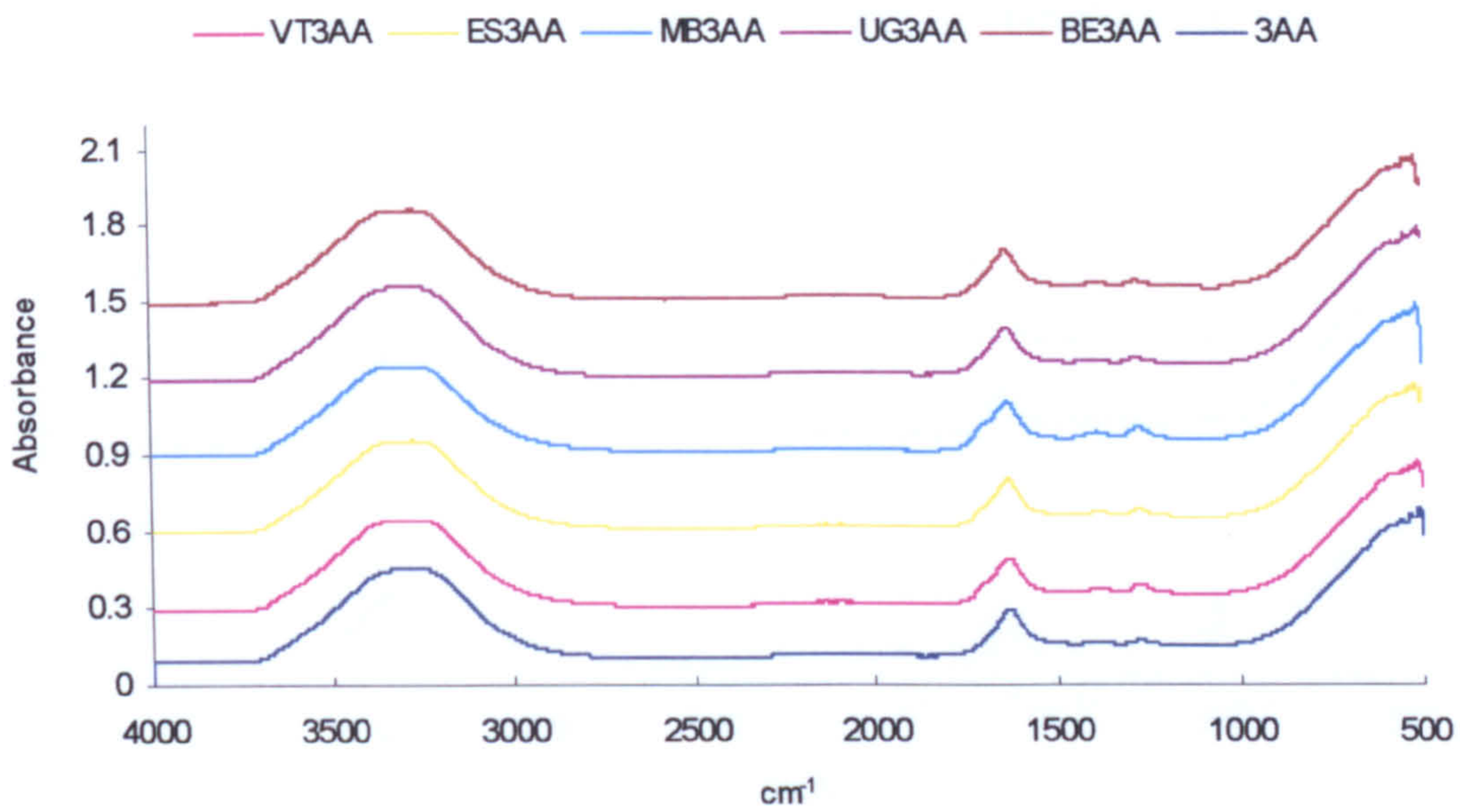


Figure 5.65 Normalized representative spectra of 3% acetic acid in which VT, ES, MB, UG and BE were stored for one year. Plots are independently offset for absorbance (absorbance scale division are 0.3 unit).

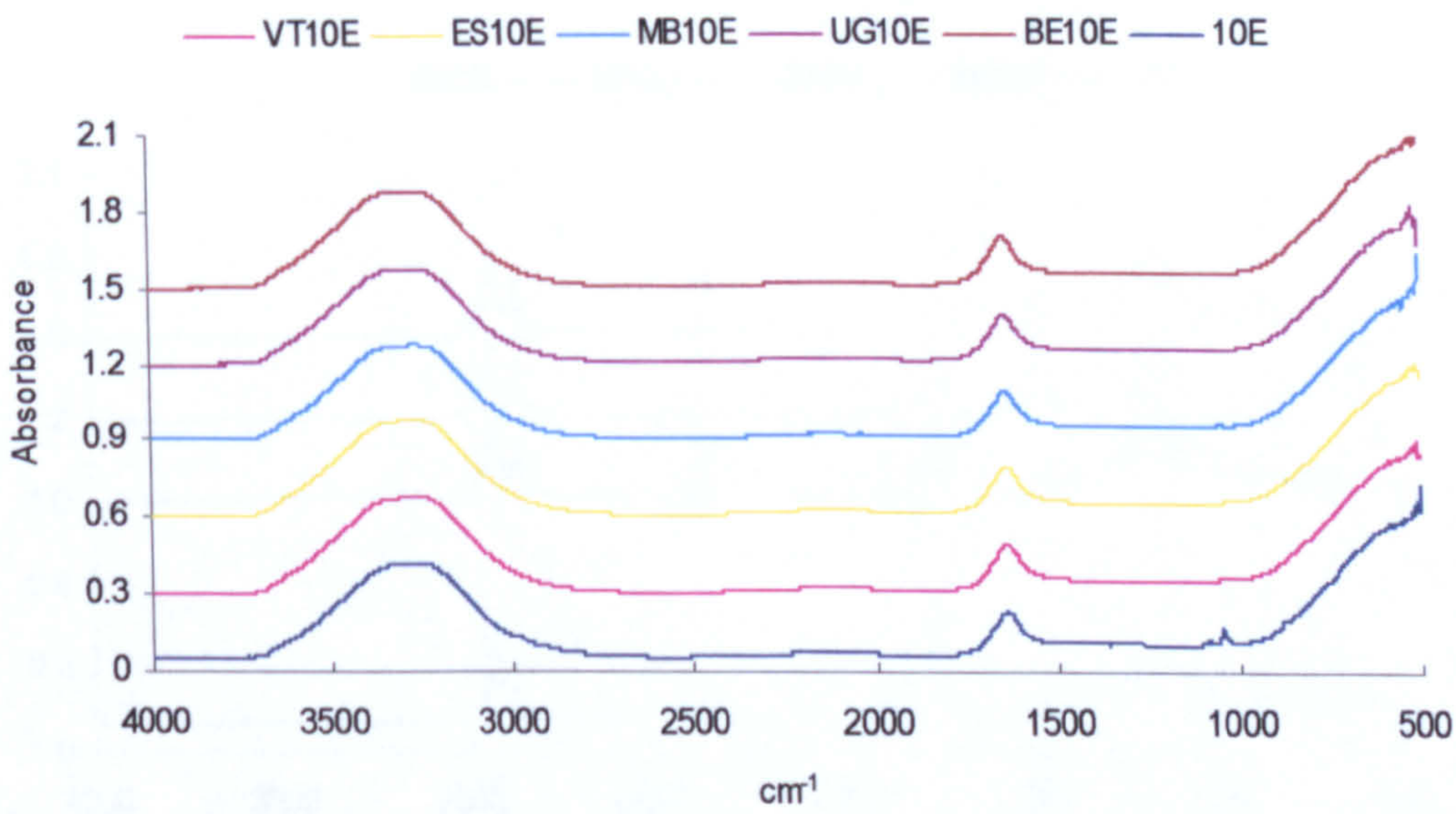


Figure 5.66 Normalized representative spectra of 10% ethanol in which VT, ES, MB, UG and BE were stored for one year. Plots are independently offset for absorbance (absorbance scale division are 0.3 unit).

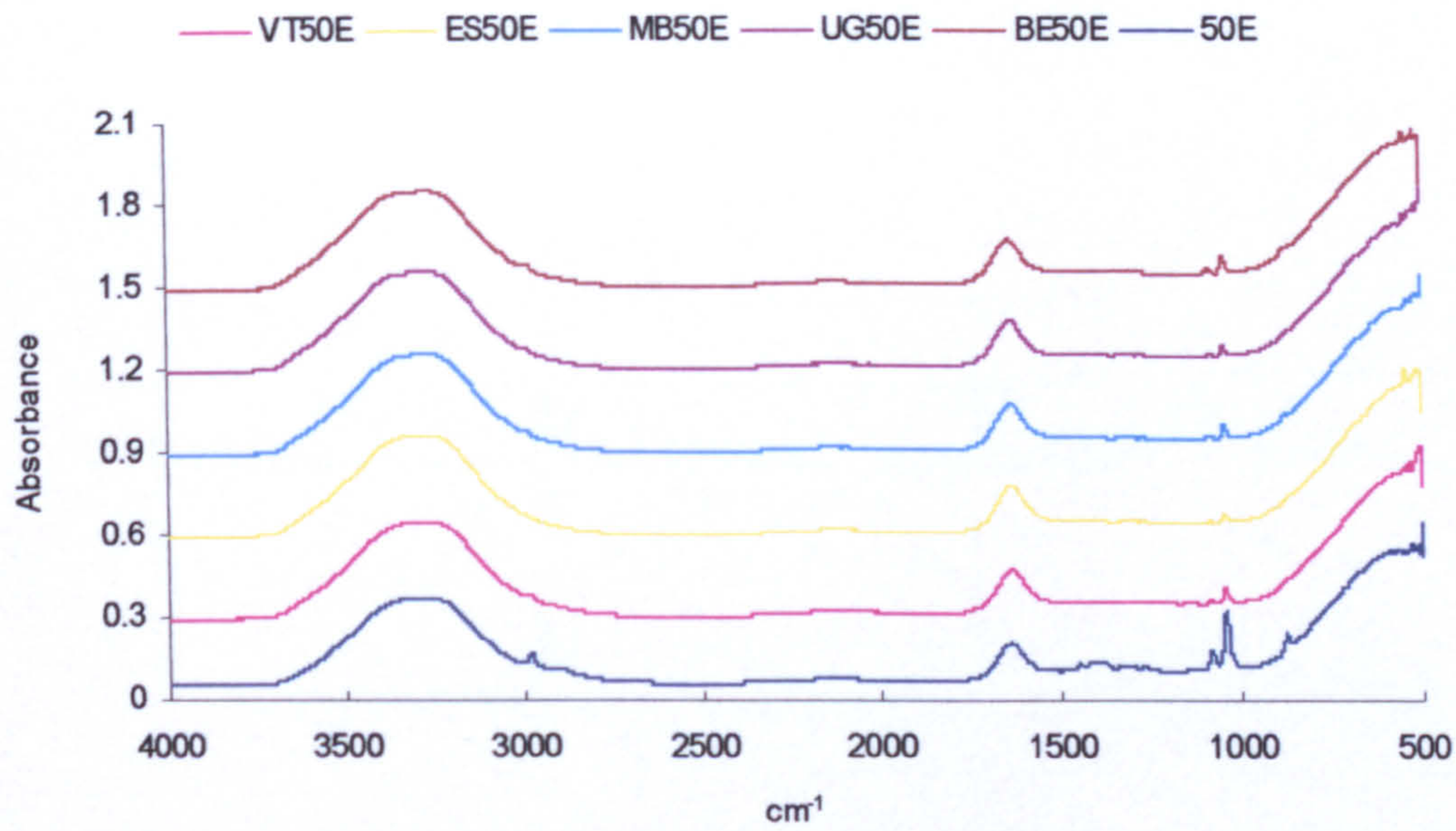


Figure 5.67 Normalized representative spectra of 50% ethanol in which VT, ES, MB, UG and BE were stored for one year. Plots are independently offset for absorbance (absorbance scale division are 0.3 unit).

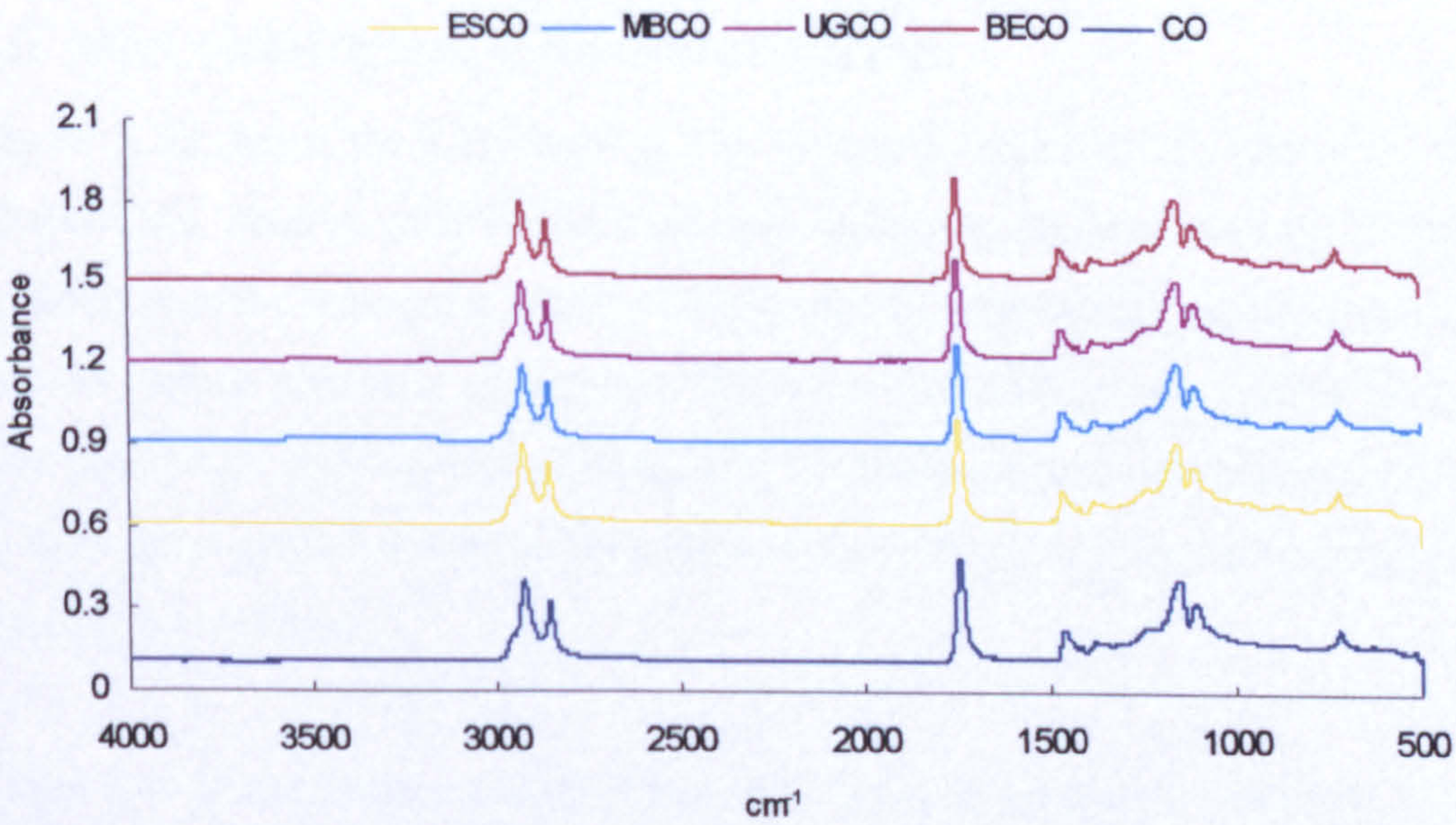


Figure 5.68 Normalized representative spectra of coconut oil in which VT, ES, MB, UG and BE were stored for one year. Plots are independently offset for absorbance (absorbance scale division are 0.3 unit).

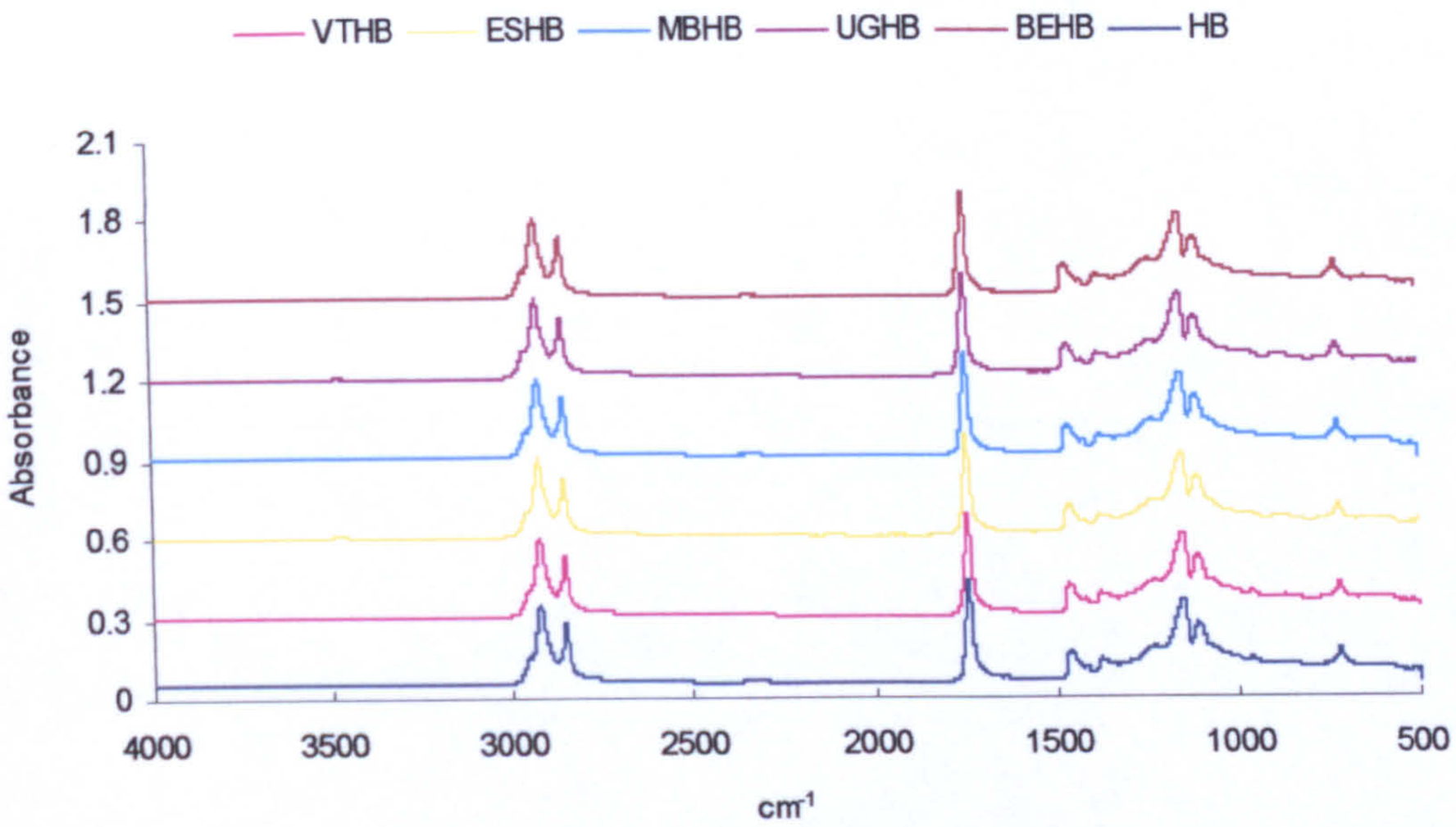


Figure 5.69 Normalized representative spectra of HB307 in which VT, ES, MB, UG and BE were stored for one year. Plots are independently offset for absorbance (absorbance scale division are 0.3 unit).

5.7 Microbiological Characterisation

Figure 5.70 shows the CFU/mm^2 (CFU: colony-forming units) adherence of *Candida albicans* on denture soft lining materials following various surface treatment. It is apparent that the maximum adherence is on the 'no treatment' control discs where there was no surface treatment carried out. When the disc surface was treated with UG sealer plus coconut oil and coconut oil alone, there is some reduction for all materials. However, in most cases greater overall adherence was observed using UG sealer, especially without coconut oil treatment.

Table 5.43 demonstrates a statistically significant difference in adhesion due to sealer, coconut oil and the materials ($P<0.05$). The effect of coconut oil was to produce a statistically significant reduction in adhesion. This reduction in adhesion also diminished the effect that sealer had on the promotion of adhesion.

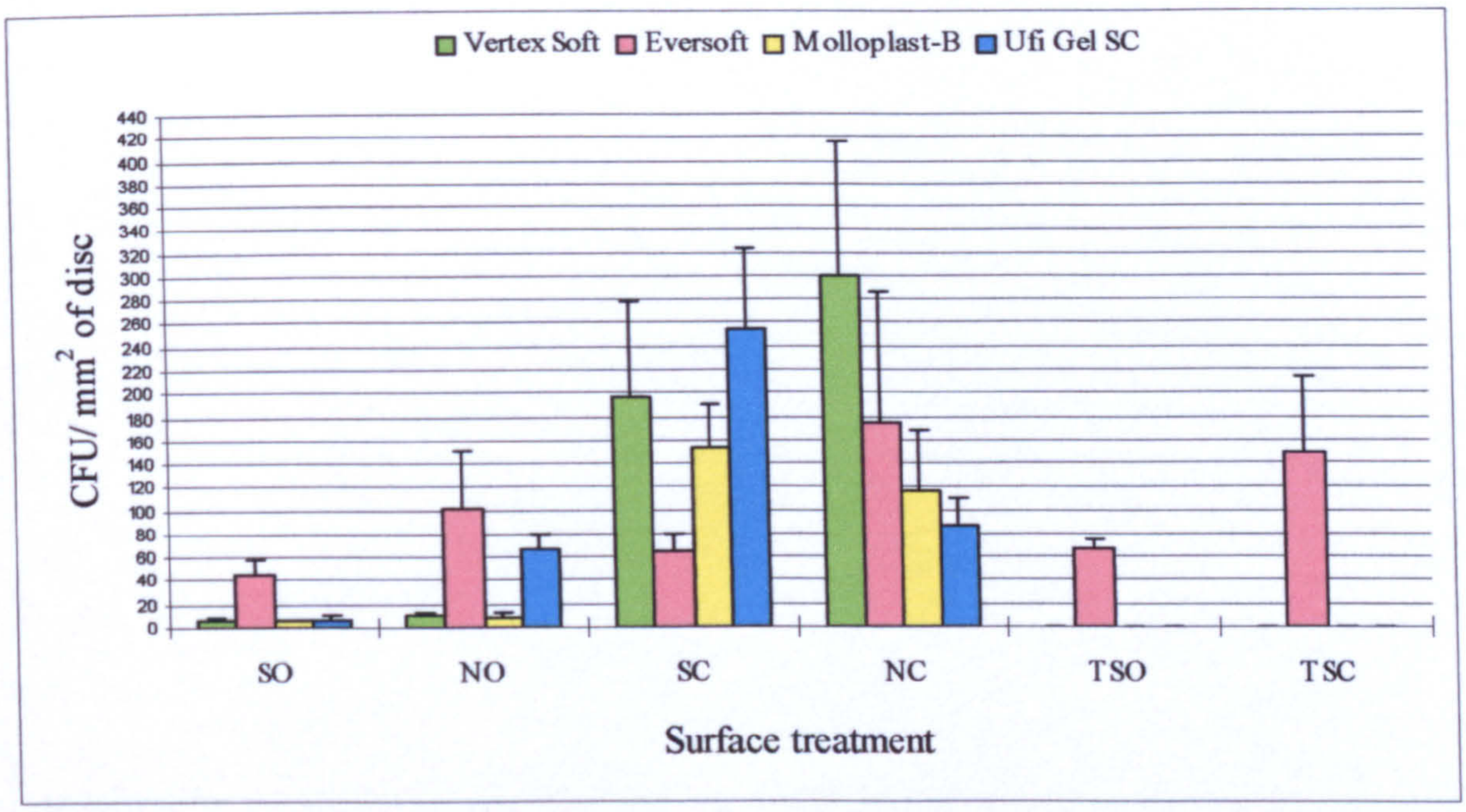


Figure 5.70 The adherence of *Candida albicans* NCYC 1467 to denture soft lining materials with varying surface treatment. (**SO**: UG sealer and coconut oil; **NO**: coconut oil only; **SC**: UG sealer only; **NC**: No surface treatment; **TSO**: ES sealer and coconut oil; **TSC**: ES sealer only)

Table 5.43 The adherence of *Candida albicans* NCYC 1467 to denture soft lining materials with varying surface treatment.

Material	Surface treatment	CFU of disc/mm^2 (s.d.)
Vertex™Soft	No surface treatment	300.6 (116.6)
EverSoft®	No surface treatment	173.9 (112.9)
Molloplast-B®	No surface treatment	116.1 (52.6)
Ufi Gel SC	No surface treatment	87.2 (22.3)
Vertex™Soft	UG sealer and coconut oil	5.9 (3.6)
EverSoft®	UG sealer and coconut oil	44.8 (12.4)
Molloplast-B®	UG sealer and coconut oil	6.2 (0.6)
Ufi Gel SC	UG sealer and coconut oil	7.1 (2.7)
Vertex™Soft	Coconut oil only	11.8 (2.2)
EverSoft®	Coconut oil only	101.4 (50.2)
Molloplast-B®	Coconut oil only	9.4 (2.8)
Ufi Gel SC	Coconut oil only	67.2 (12.5)
Vertex™Soft	UG sealer only	196.9 (81.5)
EverSoft®	UG sealer only	64.3 (15.8)
Molloplast-B®	UG sealer only	153.3 (37.1)
Ufi Gel SC	UG sealer only	253.5 (69.9)
EverSoft®	ES sealer only	149.7 (64.0)
EverSoft®	ES sealer and coconut oil	67.2 (7.9)

CHAPTER SIX

DISCUSSION

The clinical requirements (Wright, 1980a; Qudah *et al.*, 1990) of denture soft lining materials indicate that they should:

- Have low water absorption and solubility to provide dimensional stability and reduce degradation.
- Retain compliance in order to remain soft enough for the comfort of the patient.
- Retain surface integrity avoiding roughening and consequent need for replacement.
- Have good surface wettability to ensure that the surfaces are adequately lubricated by saliva to prevent frictional trauma.
- Not support fungal growth e.g. *Candida albicans* to prevent denture-related stomatitis.

In the following section the rational for the selection of the denture soft lining materials to be investigated and the methods used are discussed. Subsequently discussion of the characterisation of the materials is presented with reference to their fluid uptake, Shore A hardness, surface roughness, wettability and *C. albicans* adherence.

6.1 Selection of denture soft lining materials

In this study, four commercial denture soft lining materials and one experimental elastomer have been evaluated to determine properties, which are important in assessment of long-term degradation. The materials were of different chemical composition, physical forms and processing methods.

Two main families of polymers are used commercially as denture soft lining materials, one based on methacrylate material, the other using silicone-based technology. These can be fabricated using either heat or chemical polymerisation. The results may be influenced by material composition and chemistry as well as polymerisation mode. Hence, two methacrylate-based denture soft lining materials and two silicone-based denture soft lining materials were selected. They are representative materials to compare properties between curing type and product, and to identify the effect of various components within these materials on their acceptability as long-term denture soft lining materials.

Molloplast-B® (Wright, 1981; Qudah *et al.*, 1990; Braden *et al.*, 1995) is the most commonly used and successful heat-cured silicone-based denture soft lining material and has been used for over fifty years. It is a one-paste system of complex chemistry and is based on α-ω-dihydroxy terminated PDMS. Cross-linking is achieved by the presence of benzoyl peroxide and the application of heat. Additionally an acryloxyalkyl silane may improve bonding and the cross-linking of the silicone rubber (Wright, 1981).

In comparison to Molloplast-B®, Ufi Gel SC is a relatively new chair-side auto-cured silicone-based denture soft lining material which has not been fully investigated. Unfortunately, there is limited information to ascertain its composition. According to its technical data sheet, it is based on addition silicone technology and contains a mixture of different polyalkylsiloxanes, fumed silica, catalysts and additives (MSDS for Ufi Gel SC, 2005). This study evaluated its base and catalyst pastes in comparison with GC Reline Soft, which has a known base and catalyst composition derived from the material safety data sheet (MS346531 and MS346571, 2003). Both materials showed similar ATR-FTIR spectra. Ufi Gel SC appears to contain a form of vinyl silicone. The base paste contains a vinyl-terminated PDMS, hybride silicone as well as silicone dioxide. The catalyst paste is composed of hydrogen-terminated PDMS, platinum salt activator and additional silicone dioxide. Moreover, it also should be noted that Ufi Gel SC glazing base and catalyst are similar to the base and catalyst paste and are applied on the surface try to smooth the surface and prevent fungal penetration (SPI for Ufi Gel SC, 2000).

Unlike the silicone-based denture soft lining materials, the two methacrylate-based denture soft lining materials include plasticisers. Vertex™Soft (Brown, 1988; Qudah *et al.*, 1990; Jagger and Harrison, 1997), a heat-cured methacrylate-based denture soft lining material, has the glass transition temperature reduced by the addition of acetyl tributyl citrate (mw, 402.5), a plasticiser. It acts as a lubricant between the polymer chains, enabling them to move over each other and so allow the material to deform more easily. The secondary inter-molecular forces between the polymer chains also have the power to hold other molecules as well as acting as cohesive forces. When a solvent, or other low molecular weight material, is added to a polymer it is attracted to the chains by these

forces and gradually pushes the chains apart. If a large amount is added, the polymer will ultimately pass into solution, but if only a small amount of a non-volatile solvent is used, plasticisation occurs (Braden *et al.*, 1997).

EverSoft® (Jagger and Harrison, 1997) is marketed as a methyl-methacrylate-free methacrylate-based denture soft lining material but from its composition it would more correctly be designated a tissue conditioner. There is no monomer to be cured and the process is one of gelation. It has a reduced Tg as a result of the addition of dibutyl phthalate (mw, 278.4). Ethyl alcohol (mw, 40.1) and ethyl acetate (mw, 88.1) are added as penetrants, which speed up the process of forming a gel. When mixing the liquid and PEMA powder together, the physical change is gelation. The average particle or bead diameter was 44.0 μm with a range from 1.32 to 224 μm. During mixing the polymer beads are expanded either by ethyl alcohol or ethyl acetate to increase the spacing between the polymer chains. This swelling of the polymer structure allows the larger molecules of dibutyl phthalate to ingress. Ethyl alcohol and ethyl acetate are thought to play a combined role in transporting dibutyl phthalate into the PEMA polymer particles. Gelation occurs through a process of physical entanglement, where the polymer chains are held in a plasticiser and alcohol solution. The liquid contains no methacrylate monomer, hence there is no polymerisation reaction, and thus no risk of residual monomer irritating the oral mucosa. It should be noted that a sealer, methyl ethyl ketone (mw, 72.1), is applied to the EverSoft® surface try to provide surface smoothing and prevent contamination (MSDS for EverSoft®, 2004).

The materials currently used are either silicone or methacrylate-based systems. The common problem with the methacrylate-based materials is leaching of plasticiser which causes hardening (Braden and Wright, 1983). One solution to this problem is to use an elastomer gelled with a methacrylate monomer to produce a compliant material without the use of a plasticiser. Riggs *et al.* (2002) reported that a bromo-butyl butyl elastomer showed a good potential as a long-term denture soft lining material with low water uptake and high mechanical strength. In this study, an experimental bromo-butyl butyl elastomer was selected as it may have all the advantages of the current methacrylate-based denture

soft lining materials without the need for plasticisation, and the aim was to extend the knowledge of this material.

6.2 Selection of immersion liquids

Since denture soft lining materials are used in the mouth, they are bathed in oral fluid. In many cases, this contains a mixture of inorganic salts, organic salts and bacterial products. This may cause a variety of effects on the material in the mouth. The fluid mixture is variable and changeable due to intrinsic and extrinsic factors. Salivary composition may vary with production from gland site, and also may be influenced by other factors such as time of day and type of stimulation. It has been clearly demonstrated that changes in saliva pH depend on the rate of saliva flow. The saliva can maintain a suitable pH in the mouth by its buffering capacity (Miles *et al.*, 2004).

Natural saliva is a dilute solution, over 99 per cent being made up of water and the remaining percentage is the organic and inorganic content (Harris *et al.*, 1998). The ionic species such as bicarbonate, phosphate, sodium, chloride, potassium and magnesium provide the buffering capacity. The organic components of saliva consist of a number of enzymes, mainly esterase and α-amylase, and glycoproteins, which form the mucins in saliva, as well as a number of free amino acids, peptides, lipids and water soluble vitamins. These protect the oral tissues against infections, coat and lubricate the oral tissues and in some cases commence the digestive cycle (Miles *et al.*, 2004).

It is difficult and complex to duplicate human saliva because of the variables in composition and the unstable components of natural saliva (Leung and Darvell, 1997). This makes natural saliva itself difficult to use in *in vitro* simulation studies as this could lead to considerable variation between experimental batches. Further, long-term stability is a problem. Artificial saliva is designed to match natural saliva both in mode of action and composition. The use of artificial saliva is necessary for well-adjusted and controlled experiments. The organic and inorganic contents of saliva may have the effect of changing the osmotic gradients in any experimental procedures. The use of artificial saliva with organic components would be extremely difficult because of the long-term

degradation of the material and possible contamination. Conversely artificial saliva without organic components can be maintained during the test period without the need to be changed regularly. In this study the Fusayama *et al.* (1963) formulation which has been used for *in vitro* electro-chemical and biological tests on dental materials was chosen because it is similar to natural saliva in composition, pH, conductivity and corrosiveness (Marek, 1983).

In vitro fluid immersion may indicate the real behaviour of denture soft lining materials in everyday use. Laboratory tests usually only simulate exposure to water (Bates and Smith, 1965; Ellis *et al.*, 1977; Braden and Wright, 1983; Kazanji and Watkinson, 1988a; Kawano *et al.*, 1994b; El-Hadary *et al.*, 2000). This defines the material behaviour as a consequence of placement in an aqueous environment without any additional components. This is why distilled water is always selected to be an immersion medium to act as a control for more complex interaction with artificial saliva and food simulating liquids. However, the complexity of intra-oral use and extra oral storage of a denture soft lining material is difficult to reproduce and most *in vitro* studies have considerably simplified the process using only continuous immersion in distilled water or artificial saliva (Ellis *et al.*, 1977; Kazanji and Watkinson, 1988a). Parker *et al.* (1997) used saline solutions to study the water uptake characteristics of denture soft lining materials. However, saline solution may be a substitute for tissue or plasma fluid but cannot truly represent the complexity of oral fluids. Yanikoğlu and Duymuş (2004) adjusted the artificial saliva pH with NaOH or HCl to try to simulate neutral, acidic and basic saliva. However, their solution's composition is confusing since there is no evidence to support the solution as an oral fluid or a food simulating liquid. Denture soft lining materials in use in the mouth are not only bathed in saliva, but also in foods and drinks. Hence, the ability to define how each component of saliva and food might affect the denture soft lining material is important.

Two authors (Wu *et al.*, 1982; Yap *et al.*, 2003) have previously selected FDA food simulating solvents as representative of the action of food in the mouth. However, in 2002, the FDA revised the guidelines on food simulating liquids. Currently the

recommendations are as follows. 10 per cent ethanol is the equivalent to aqueous or low-alcoholic food. 50 per cent ethanol is a representation of high-alcohol food. Coconut oil and HB307 are representative of fatty foods. 50 per cent ethanol and oils seem a little excessive but in the FDA view, a material which passes this test is suitable to use in mouth in the longer term. It is really designed to give an accelerated evaluation for what might happen over five or six years of clinical use. In addition, 3 per cent acetic acid is recommended as an acidic food stimulant by the EC Food Contact Legislation (2000).

Certainly, previous *in vitro* investigations of long-term denture soft lining materials have not clearly explained the differences in laboratory and clinical findings (Ellis *et al.*, 1977; Kazanji and Watkinson, 1988a; Jepson *et al.*, 1993a; Murata *et al.*, 1996; Jepson *et al.*, 2000). In this study a total of seven immersion solutions were selected, because these solutions are the most clinically relevant in the mouth. The objective of this study was to gain an understanding of the effect of food additives or food simulants on the materials. It may also used in understanding which solutions have the greater influence on materials in the oral cavity.

6.3 The interaction between denture soft lining materials and food simulating liquids: fluid uptake properties

In clinical dental applications, the denture soft lining material lies between the hard denture base and the tissues. It will be exposed to the oral fluids which fill the space between the denture and the soft tissue. Hence, most studies involve the immersion of samples in a fixed volume of fluid which remain unchanged for the duration of the experiment for convenience of experimental method (Ellis *et al.*, 1979; Braden and Wright, 1983; Kazanji and Watkinson, 1988a). This is most representative of cases when oral fluid stagnates between the denture and the oral tissue. However, denture mobility, especially in the mandible, allows free flow of saliva and extrinsic fluids over the fitting surface of the denture. In addition, part of the denture soft lining material at the junction with the hard base and also forming the border of the denture is directly in contact with food as well as saliva. Moreover, the denture is removable and may be soaked in water or solutions of denture cleaners at night or sometimes may be stored dry. In order to

consider these conditions, the effects on these materials when immersed in solution which was both unchanged and also changed at regular interval were evaluated. Changing the immersion solution at regular intervals is closer to oral condition where oral fluid is constantly replaced. The solutions which were changed regularly include distilled water, artificial saliva, 3 per cent acetic acid, 10 per cent ethanol and 50 per cent ethanol to maintain concentration. This methodology has not previously been used in evaluation of denture soft lining materials.

In this study, the gravimetric method established by Braden (1964) was employed to determine the fluid absorption characteristics of the test materials. This method has been applied extensively to conventional methacrylate-based denture materials (Braden, 1968), composite resins (Braden and Clarke, 1984) and denture soft lining materials (Braden and Wright, 1983; Kalachandra *et al.*, 1995; Waters *et al.*, 1996). Variations in the results were resolved by using six samples for each material in each medium. The results were plotted as the percentage weight changes with the square root of time. For this method, the specimens are desiccated initially to remove the small amount of water present following the fabrication process. The specimen is then immersed in the test medium and weighed at predetermined intervals. During this process, the specimens absorb water and/or fluid. To avoid confusion where simultaneously, loss of material and fluid uptake can give an apparent null result, specimens were desorbed at the final stage to ascertain percentage weight loss (solubility) and real percentage uptake. Under normal conditions, it is assumed that at equilibrium, when the weight is constant, all soluble matter has been lost and the specimen is saturated with water/fluid (Braden and Wright, 1983).

Identified variables which may interfere with the experiment were controlled to reduce variance of the results. Firstly, the powder and liquid portions of Vertex™Soft and EverSoft® were accurately weighed before mixing to ensure the consistency of powder/liquid ratio. Variation in this ratio would result in the variation of the amount of fluid uptake and solubility because the liquid contains the plasticiser. Hence, increasing liquid volume may cause proportionally more plasticiser loss (Muruta *et al.*, 2001). Secondly, the specimens were cured as recommended by the manufacturer to provide

manufacturer's recommended level of polymerisation. Finally, during each weighing cycle, each specimen was removed at predetermined time intervals using tweezers. Gloves were worn to prevent surface contamination, and each disc carefully blotted to remove excess surface liquid using filter paper. All weighing was carried out within thirty seconds of removal from the fluid. This reduces the risk of loss of water close to the surface.

Diffusion of small molecules into polymeric materials can be accompanied by a variety of processes including swelling, release of elastic stresses, and onset of fracture (Rossi, 1996). Fedors (1980) reported the crack formation in epoxy resins. It was hypothesised that water uptake swells the resin and strains molecular bonds to cause internal rupture of the resin. There are other internal pressures which can initiate sample cracking, which are attraction of water to the impurities, shrinking during curing and thermal contraction from the cure temperature to room temperature. Turner (1987) reported on studying water absorption of PMMA that the difference in water absorption with different molecular weight polymers was mainly due to microvoids which can be caused by imperfect packing of the polymer chains in the polymerisation process leading to trapped air and polymerisation shrinkage. An additional droplets theory suggests that the presence of hydrophilic groups is thought to have a similar effect of encouraging water uptake via polar attraction (Fedors, 1980). The material may creep around the droplet which is growing under a constant stress. The action of creep would relax the restraining force and extend the absorption process. The material will absorb a greater amount of water depending on the particular creep characteristics of the material (Riggs, 1997).

6.3.1 Silicone-based denture soft lining materials

Molloplast-B® has been investigated in previous studies and the percentage of water absorption has been variously reported as 3.8 per cent over 30 days by Bates and Smith (1965), 1.73 per cent over three months by Suchatlampong *et al.* (1976) and only 0.43 per cent for up to eight months by Kazanji and Watkinson (1988a). In this study, Molloplast-B® showed a small water absorption value (3.08 per cent) when stored in distilled water

after one year. The differences may be the result of different processing methods, specimen volumes, and periods of immersion in the different studies.

The water absorption data obtained were checked for evidence of Fickian-type diffusion during immersion. For diffusion to be Fickian, plots of M_t/M_∞, mass at time t over the mass at equilibrium would be equal to 0.5, and M_t/M_∞ against $t^{1/2}$ would yield a straight line. Logarithmic plots of data yielded gradients greater than 0.5. Case II diffusion gives a slope of 1.0, attributable to molecular relaxation, but is still explicable in terms of Fick's Laws expressed in terms of chemical potential (Thomas and Windle, 1982).

The form of water uptake of Molloplast-B® and Ufi Gel SC in distilled water is in a Fickian diffusion manner. Water goes into the silicones, from two separate fronts on the major surfaces of the material, then wets the soluble particles. There is a dependence on the hydrophilic nature of both the soluble particles and the matrix. If the soluble particles are highly soluble with a high osmotic potential and the absorbance of the matrix is very small then the growth of the droplet can dominate the early uptake characteristics and result in a steep concentration front diffusing into the material. Here the soluble particles in Molloplast-B® and Ufi Gel SC seem to have a lower osmotic potential associated with them so in the initial stages their effect is less, and they do slow the rate of diffusion. A normal Fickian front moves into the material with the concentration quickly reaching what looks like near saturation of the matrix. The expansion of the droplets then comes to dominate the uptake into the material, with a near uniform concentration profile across the sample. The droplets will keep expanding until the restraining force exerted by the material is equal to that resulting from the osmotic driving force. If the material creeps around the droplets, it causes the continuing expansion of the droplets, and then a non-equilibrating continuous uptake results. Also, if this expansion of the droplets leads to fracturing of the material around the droplets, it would cause the formation of a crack network, then a non-equilibrating intermittent uptake results. Indeed, Molloplast-B® and Ufi Gel SC in distilled water demonstrate the normal elastic restraint with the overall kinetic looking fairly Fickian, and shows an equilibrium between restraining force and osmotic force. Both Molloplast-B® and Ufi Gel SC also show a similar trend in AS, 3AA,

10E, and 50E, which suggests that these kinds of aqueous food simulating liquids have no influence on the uptake behaviour of similar materials when immersed in solution. Moreover, long chain fatty acid (CO and HB) initially drive the diffusion process faster than in the above aqueous solutions. However, this rapid fluid absorption could not promote the rate of droplet growth and only open up minor communication with the surface of the material leading to slow loss of soluble substances. This would explain the equilibrium in weight from one week to one year. All these results confirm Molloplast-B® and Ufi Gel SC are extremely stable chemically.

This is further related to the mechanical properties of Molloplast-B® and Ufi Gel SC. Wright (1981) suggested Molloplast-B® crosslinked by heat may demonstrate better bonding to the filler, and this coupled with the application of pressure produces a dense material. Moreover, Molloplast-B® does not contain a plasticiser and this would be a contributory factor to low water/fluid absorption. Previous work (Wright, 1980a; Kazanji and Watkinson, 1988a) with other cold-curing silicone-based denture soft lining materials have demonstrated marked percentage absorption either in distilled water or in artificial saliva. However, such absorption was not found in this study for Ufi Gel SC. In fact, the former cold-curing silicone-based denture soft lining materials were of the condensation curing type (Flexibase). Riggs (1997) suggested such condensation silicone materials are always going to be prone to scission and recombination of the siloxane bond which leads to leaching of the silicone. However, Ufi Gel SC is an addition curing hydrosilyised silicone. Fumed silicas are used in reinforcing silicones, as they have a very small particle size, between 4 and 12 nm, in terms of surface area ranging from 50 and 300 m^2g^{-1} (Riggs, 1997). Riggs (1997) also suggested that the excess of the hydrogen terminated siloxane bonded to the silica surface not only improved the strength of the material but may reduce the fluid uptake. It is interesting to note that Molloplast-B® and Ufi Gel SC, despite the different curing method and composition, show no significant differences in their fluid absorption, solubility and real uptake characteristics.

Wright (1981) reported the solubility of Molloplast-B® was less than 2.17 per cent in distilled water up to 176 days. In this study, both Molloplast-B® and Ufi Gel SC

exhibited small solubility values either in unchanged or changed liquids. However, they do not exactly follow the normal pattern since after desorption the net weight is larger than the original weight. Suchatlampong *et al.* (1976) suggested that some water was permanently incorporated into the Molloplast-B® as she also could not achieve the original weight of the sample on desorption. The results in this study are probably a combination of material swelling, retention of water/fluid and loss of substances. A full explanation of the fluid absorption behavior of silicone-based denture soft lining materials requires a detailed analysis of the various inorganic fillers found in these materials. Suchatlampong's suggestion to heat the specimen to try to remove incorporated water has not been carried out in this investigation.

6.3.1.1 Differences between unchanged and changed immersion regimes

As previously described, in order to cover all possible conditions, both unchanged and changed immersing regimes were used. Unchanged immersion is most representative of cases when oral fluid stagnates between the denture soft lining materials and the oral tissue. Changed immersion is more representative of the mouth where oral fluid is constantly replaced. The osmotic pressure of the external solution may affect water/fluid uptake of the material. With unchanged solution, the leachable substances leached into the external solution and reacted with the external solution until saturation. However, with changed solution, this saturation will not occur due to continual external addition of fresh solution, thus accelerating the diffusion and loss process.

For Molloplast-B® and Ufi Gel SC, significant differences could not be shown between unchanged and changed immersion fluid with the real uptake always being slightly less at six months (changed) than at one year (unchanged). The weight change, solubility and real uptake are generally so small that the differences seen would not be clinical relevant. Once again, these results confirm that Molloplast-B® and Ufi Gel SC would not be affected by the osmotic pressure of external solutions; present little soluble/hydrophilic components within the materials; and have stable mechanical properties under chemical presence in the environment (e.g. water, artificial saliva, organic solvents, etc.)

6.3.1.2 Clinical implications

Immersion in distilled water or artificial saliva does not produce the magnitude or the speed of change in the properties of Molloplast-B® and Ufi Gel SC seen clinically. 3 per cent acetic acid, 10 per cent ethanol, 50 per cent ethanol, coconut oil and HB307 may help to accelerate changes and simulate the effect of oral fluids. However, both Molloplast-B® and Ufi Gel SC are still the most stable products. These results confirm that Molloplast-B® and Ufi Gel SC are able to resist weak acids, alcoholic drinks and fatty foods whilst maintaining the integrity of their three-dimensional cross-linked structure.

The real percentage uptake of Molloplast-B® and Ufi Gel SC in all liquids is less than reported for the acrylic base material (2.2 per cent) (Bates and Smith, 1965). Briefly, Molloplast-B® and Ufi Gel SC offer ideal fluid absorption characteristics to provide dimensional stability and reduce degradation in all liquids although they were of different composition and method of polymerisation.

Compared to Molloplast-B®, Ufi Gel SC is quick and easy to use being supplied in a form which allows direct injection of the auto-mixed material onto the prepared surface. However, the achievement of a uniform thickness of a chemically polymerised silicone-based denture soft lining material at the chair-side is still a challenge.

6.3.2 Methacrylate-based denture soft lining materials

It is noted that the basic structure of Vertex™Soft and EverSoft® is quite different although both materials used as denture soft lining materials are blended with plasticisers to lower T_g. A lower T_g allows for greater polymer chain mobility, thus producing a more flexible material. They use similar PEMA powder but different bead size. Vertex™Soft liquid is blended with methyl methacrylate, acetyl tributyl citrate and an unknown crosslinker to produce a soft polymer (Vertex-dental B.V., 2003; Jagger and Harrison, 1997). However, EverSoft® liquid is a mixture of dibutyl phthalate, ethyl acetate and ethyl alcohol to make a soft polymer-gel material (MSDS by Dentsply Austenal, 2003;

Jagger and Harrison, 1997). Theoretically, the plasticisers (e.g. DBP and ATBC) are polymers that do not chemically interact with the polymer matrix, but simply reside within its folds as a lubricant and reduce entanglements, thus softening the polymer. These molecules are unattached and will eventually diffuse out of the polymer. When the plasticiser gradually leaches into an immersing fluid, the polymer chains can then move closer and improve their interactions, causing the material to harden. However, small molecules (e.g. water or ethanol) also have their plasticizing effect (Ferracane, 1995).

Braden and Wright (1983) have suggested the methacrylate-based denture soft lining materials undergo two processes simultaneously when immersed in water, plasticisers and other soluble substances are leached into the water, and water is absorbed by the polymer. The balance between these two processes affects both the dimensional stability and compliance of the materials. It seems likely that the methacrylate-based denture soft lining materials would follow the standard theory for uptake and release of soluble material which is based on the effect of an impurity or soluble structure in the material. What would happen when water/fluid is absorbed? The water/fluid would dissolve the impurity causing expansion which pressure will cause the material either to gradually crack if the material is rigid or expand if the material is flexible. The latter probably occurs in denture soft lining materials. This may create a pathway for the soluble substance or plasticiser to migrate out of the material.

Basically, distilled water is used as a useful guide to the diffusion process without the complication of the osmotic effect of a solution. In this study, the apparent percentage absorption for Vertex™Soft and EverSoft® of distilled water after one year was 3.1 per cent and 4.8 per cent respectively. However, the percentage solubility of EverSoft® (13.5 per cent) was ten times larger than Vertex™Soft (1.3 per cent). Although Vertex™Soft water absorption has not been reported previously, it should follow the trend for a heat-cured methacrylate-based denture soft lining material. The structural stability of heat-cured methacrylate-based material is superior to chemical-cured and gel-form materials. This would explain the larger real percentage uptake of gel-form EverSoft®. The absorption and solubility results for EverSoft® were similar to those reported by Parr and

Rueggeberg (1999) for PermaSoft® (supplied by Dentsply Austenal International., USA, is the American brand name for EverSoft®).

Both Vertex™Soft and EverSoft® show a similar trend in DW and 10E, which suggests that these kinds of aqueous food simulating liquids have no influence on the uptake behaviour of similar materials when immersed in solution. However, both materials show a different trend in AS, 3AA, 50E, CO and HB, driving the diffusion process faster than in the above aqueous solutions. This rapid fluid absorption or loss could promote the rate of droplet growth and open up more communication with the surface of the material leading to loss of soluble substances. All these results confirm Vertex™Soft and EverSoft® are not stable chemically.

Vertex™Soft and EverSoft® also show an initial high rate of uptake followed by a slower rate which continues throughout the measured time period. In distilled water, this continuous water uptake indicates continued droplet growth which the methacrylate-based materials are unable to restrain. This may be explained by the viscoelastic nature of the materials under low rates of strain at 37±1°C, which would be expected to creep resulting in steady droplet growth (Parker *et al.*, 1999).

As previously described, if the soluble particles are highly soluble with a high osmotic potential and the absorbance of the matrix is very small then the growth of the droplet can dominate the early uptake characteristics and result in a steep concentration front diffusing into the material. A non-Fickian front moves into the material with the concentration impossibly reaching what looks like near saturation of the matrix. The expansion of the droplets comes to dominate the uptake into the material. The droplets will keep expanding until the restraining force exerted by the material is equal to that resulting from the osmotic driving force. However, if the material creeps around the droplets, it causes the continuing expansion of the droplets, and then a non-equilibrating continuous uptake results. Also, if this expansion of the droplets leads to fracturing of the material around the droplets, it would cause the formation of a crack network, then a non-equilibrating intermittent uptake results.

6.3.2.1 Further analysis of possibly leached substances

For Vertex™Soft the percentage solubility was only 1.3 per cent and may be attributed to unreacted monomer, unknown crosslinker and a little amount of ATBC. However, for EverSoft® the percentage solubility was much greater at 13.5 per cent and cannot be only attributed to the loss of ethyl alcohol and ethyl acetate (from the manufacturer's information, the percentage of dibutyl phthalate, ethyl alcohol and ethyl acetate in the liquid is a range from 17.1 per cent to 25.7 per cent, 1.4 per cent to 4.3 per cent, and 0.3 per cent to 2.9 per cent respectively, which using powder/liquid ratio of 2.5:1 is equivalent to less in the mixed material). Therefore leaching out of some dibutyl phthalate from the gel-matrix into water must occur.

It would be expected that shrinkage would occur when the percentage solubility was higher than the percentage absorption. This is why the EverSoft® specimens showed a shrinkage.

Vertex™Soft and EverSoft® show reduced absorption from artificial saliva and seem to reach an early equilibrium. As in previous reports (Ellis *et al.*, 1977; Kazanji and Watkinson, 1988a), the solubility of the methacrylate-based denture soft lining materials was different during immersion in artificial saliva or distilled water. These results support the theory that the fluid uptake is osmotically driven. In ionic solutions the driving force is reduced and therefore the restraining force from the material is able to limit droplet growth leading to osmotic and restraining force reaching balance quickly. The reduced driving force will also result in less creep (Parker *et al.*, 1999). Thus, artificial saliva as an ionic solution reduced fluid absorption due to osmotic gradients.

In 3 per cent acetic acid, Vertex™Soft and EverSoft® have higher uptake than in distilled water and artificial saliva. It seems likely that acetic acid diffuses more readily into the materials than water. It is unlikely that materials exert a lower restraining force on the droplets, so allowing them to grow more readily, and it is possible that the fluid soluble components result in a higher osmotic potential to drive the uptake (Parker *et al.*, 1999).

In 10 per cent ethanol after one year, the apparent absorption for Vertex™Soft and EverSoft® was 3.2 per cent and 7.0 per cent respectively. After desorption, the solubility in 10 per cent ethanol for Vertex™Soft and EverSoft® was 0.9 per cent and 13.5 per cent respectively. There is no significant difference in comparison to specimens immersed in distilled water. The absorption may be explained by the droplets theory as described in the above aqueous solutions. Moreover, this result leads to speculation. Firstly, in 10 per cent ethanol, water would predominate the diffusion process rather than ethanol. 10 per cent ethanol is fully miscible in 90 per cent distilled water and the proportion of ethanol is not enough to lead the diffusion process. Secondly, the mixture of distilled water with ethanol would lead to more fluid absorption in a gel-form material than in a heat-cured material but would not leach more substances in comparison to in distilled water. Overall, the fluid uptake behaviour of methacrylate-based denture soft lining materials in 10 per cent ethanol is similar to in distilled water.

A cyclical change in weight occurred for Vertex™Soft and EverSoft® immersed in 50 per cent ethanol, caused by the higher absorption and solubility. This may be explained by combining visual observations with the time based weight changes. A rapid fluid uptake is observed during the first six hours indicative of ethanol and/or water absorption outweighing the loss of substances in the 50 per cent ethanol. Although ethanol is miscible in water, in 50 per cent ethanol, ethanol would predominate the diffusion process. Ethanol would initially drive the diffusion process faster than in the above aqueous solutions. However, this rapid fluid absorption promotes the rate of droplet growth and opens up communication with the surface of the material leading to more rapid loss of soluble substance or plasticiser. This would explain the rapid loss in weight from one day to one week. Moreover, firstly, an undulating distortion of the sample was observed from day one till day three. This undulating distortion could be explained either by the viscoelastic properties of the material resisting rapid droplet formation and osmotic pressure or by relief of processing stresses. The latter phenomenon is when a natural dimensional change is inhibited, the affected material contains stresses. If stresses are relaxed, a resultant distortion or warpage of material may occur. This principle is important in the fabrication of heat-cured denture bases, because stresses invariably are

induced during processing (Anusavice, 1996). Secondly, a shrinkage of the specimens was seen after one week until one month. This would occur if the percentage solubility was higher than the percentage absorption during this period. Vertex™Soft and EverSoft® weight loss was 9.5 per cent and 14.5 per cent at one month respectively, and their final percentage solubility was 6.3 per cent and 12.4 per cent respectively in 50 per cent ethanol. The amount of residual monomer, unknown crosslinker, ethyl acetate and ethyl alcohol are not enough to account for the amount of loss in weight. Plasticisers may also be lost from both Vertex™Soft and EverSoft®. However, after two months of immersion a gradual increase in weight occurs. The net percentage weight increase was 4.6 per cent and 6.8 per cent respectively at one year. A number of possible factors could be responsible for this unusual pattern of weight increase. Firstly, it may be explained in terms of a changing balance between osmotic gradients and the restraining nature of the material. At two months, 25 ml of fresh 50 per cent ethanol solution was added to maintain a fixed volume, following the evaporation of ethanol in the incubator and the process of measurement. As in the initial stage of the experiment, ethanol would be absorbed quickly and cause an increase in weight again. Secondly, when the plasticiser leaches into the ethanol/water solution, the plasticiser would be dissolved in ethanol until saturation. When the ethanol is saturated, the plasticiser would no longer have any osmotic pressure to leach into the external solution.

Furthermore, both Vertex™Soft and EverSoft® lost from 15 per cent to 24 per cent in weight on storage in coconut oil and HB307. As the amount of residual monomer and unknown crosslinker in Vertex™Soft, and ethyl alcohol and ethyl acetate in EverSoft®, would not account for the loss in weight observed it is assumed that leaching out of acetyl tributyl citrate and dibutyl phthalate during immersion in coconut oil and HB307 occurs. It should be noted that during this process their hardness values increased significantly. The loss of plasticisers cannot be replaced by the immersing oil because of the long-chain molecules of the oils.

6.3.2.2 Differences between unchanged and changed immersion regimes

Generally, for Vertex™Soft, significant differences in the percentage absorption between unchanged and changed immersing regimes could not be demonstrated except when immersed in 50 per cent ethanol. However, in AS the relative osmotic pressure during the fluid absorption and solubility lead to a changing balance between weight gain and loss. Between six months and one year weight loss is observed so that at six months the real uptake is greater than at one year. A similar results was observed by EverSoft® in AS.

A cyclical weight change also occurred for Vertex™Soft and EverSoft® immersed in changed 50 per cent ethanol, caused by the higher absorption and solubility. However, unlike unchanged solution a final loss in weight at six months was observed in Vertex™Soft and EverSoft® for the changed solution. A number of possible factors would be responsible for this difference. Firstly, it is noted that both DBP and ATBC would dissolve in ethanol. The changed solution maintains the concentration of ethanol in the liquid. This will increase the effect of the ethanol diffusing into the polymer matrix to lead droplet growth and formation and the plasticiser is continuously leaching out and dissolving in ethanol. With unchanged solution, when the plasticiser leached into the ethanol/ water solution, the plasticiser would be dissolved in ethanol only until saturation. However, in changed solution this saturation will not occur due to continual external addition of fresh solution, thus explaining the continuous loss in weight for Vertex™Soft and EverSoft®. Generally, it seems that the changed 50 per cent ethanol encourages loss in weight of methacrylate-based denture soft lining material.

As expected, the real percentage uptake of heat-cured Vertex™Soft is less than the gel-form EverSoft® in either changed solution or unchanged solution. This would be explained by the different polymer structure and polymerisation of Vertex™Soft. With changed immersion fluid, saturation in the external solution is difficult to reach due to regular provision of fresh solution, which may accelerate the diffusion and loss process.

6.3.2.3 Clinical implications

Immersion in distilled water, artificial saliva or 10 per cent ethanol do not produce the magnitude of change in the properties of methacrylate-based denture soft lining materials observed clinically. However, 3 per cent acetic acid, 50 per cent ethanol, coconut oil and HB307 do cause more significant changes. The methacrylate-based denture soft lining materials are not stable products. They absorb more liquid in weak acids, and leach more plasticiser with high alcohol and fatty foods. Hence, weak acids, high alcohol and fatty foods may cause the effects seen clinically.

Compared to Vertex™Soft, EverSoft® is only suitable for short-term use as a tissue conditioning material. Generally, dimensional instability would be the major problem for methacrylate-based denture soft lining materials.

6.3.3 Experimental bromo-butyl butyl elastomer

Butyl elastomers are renowned for their resistance to oxidation and weathering and have a low permeability (Brydson, 1988). The major variation on the butyl elastomers is bromide halogenation which is used primarily to raise the polarity of the chain to promote adhesion to different substrates and improve the compatibility with other polymers when forming blends. This experimental elastomer used a bromo-butyl elastomer gelled with a butyl methacrylate monomer crosslinked with ethylene glycol dimethacrylate and initiated with lauroyl peroxide to produce a compliant material without the use of a traditional plasticiser.

Bromo-butyl butyl elastomer has been investigated by Riggs *et al.* (2002) and the apparent water absorption and solubility were 3.37 per cent up to 203 days and 0.31 per cent, respectively. In this study, BE showed 6.40 per cent apparent water absorption up to 364 days and a nearly insoluble value after desorption. Basically, the values fitted Riggs *et al.* (2002) results. However, water/fluid uptake was problematic in this study due to high uptake data in the other six food simulating liquids. Not only did BE have a high uptake in the five aqueous food simulating liquids, it also suffered from degradation in the two oil environments.

In the five aqueous liquids, this would be explained by droplet theory. The bromo-butyl butyl elastomer has a number of water/fluid soluble impurities, and as water/fluid diffuses through the polymer matrix, the particles dissolve to form droplets containing an aqueous solution of the impurity, which exerts an osmotic pressure. This causes the droplets to grow, generating elastic stresses around the droplet. The process equilibrates until osmotic and elastic forces balance, unless these forces cause the polymer to fracture. Hence, this continued uptake has been attributed to droplet growth related to the presence of water/fluid soluble or hydrophilic components in the material (Riggs *et al.*, 2001). The uptake of the bromo-butyl butyl elastomer is still higher than might be expected and the increase of polarity due to halogenation has been suggested to increase the water/fluid uptake (Riggs *et al.*, 2002).

Notably the BE showed an increased weight gain in changed AS despite the shorter six months period. This was similar to that observed for Vertex™Soft and EverSoft® and may also be explained by different osmotic gradients. A similar but less dramatic effect was noted with 50E which was different from Vertex™Soft and EverSoft® because of the lack of soluble components in BE. Again different osmotic gradients may be operating.

It is also noted that the bromo-butyl butyl elastomer showed a marked swelling in the two oil environments. The greater the absorption of oil, the greater will be the associated swelling, loss of strength, dimensional change and possible structural damage allowing easier oil ingress. Furthermore, constituents leaching from the polymer network may facilitate oil uptake by disrupting the polymer matrix, and giving rise to a network more easily penetrated by oil. The bromo-butyl butyl elastomer maybe unable to resist fatty foods which also may damage the integrity of their three-dimensional cross-linked structure.

6.3.4 Summary of uptake characteristics

This study, using gravimetric measurements, determined the fluid uptake characteristics of denture soft lining materials immersed in either unchanged or changed food simulating liquids.

Percentage weight gain, solubility and real fluid uptake for methacrylate-based denture soft lining materials and bromo-butyl butyl elastomer were significantly greater than silicone-based denture soft lining materials. The fluid sorption characteristic of Ufi Gel SC is close to Molloplast-B®. The fluid uptake characteristics of Vertex™Soft and EverSoft® lie between bromo-butyl butyl elastomer and silicone-based denture soft lining materials.

The immersion of Vertex™Soft and EverSoft® in regularly changed 50 per cent ethanol, coconut oil and HB307 does cause degradation similar to that seen during intra-oral use. However, the immersion of Vertex™Soft and EverSoft® in all unchanged food simulating liquids except oils does not cause marked degradation. In addition, the immersion of Molloplast-B® and Ufi Gel SC either in unchanged or changed food simulating liquids caused minimal changes. The bromo-butyl butyl elastomer is not suitable for immersing in oils due to loss of strength caused by chain scission.

Furthermore, changed 50 per cent ethanol might be the most suitable solvent presently used to simulate oral fluids because it most closely reproduces changes which have been observed for soft linings in clinical use.

6.4 The interaction between denture soft lining materials and food simulating liquids: Shore A hardness and compliance

6.4.1 Validity of the method

In clinical use, measuring the cushioning ability of a denture soft lining material is relevant as this is the property which makes the patient more comfortable. Using an indentator to measure the force necessary to cause a displacement from the point of pressure is a valid and realistic method of measurement being comparable to the effect of a bony prominence intra-orally. Hence, the hardness values were determined with a Shore A hardness instrument to measure the compliance of the elastomeric material.

Kazanji and Watkinson (1988b) suggested that a thickness of denture soft lining material of between 2 and 3 mm was most appropriate to provide suitable compliance for clinical use. However, Hayakawa *et al.* (2003) used 10 mm thick samples to test hardness. Durometer measures depended on the thickness of the liner and the properties of the supporting base. In this present study, the focus was the sample size that could reflect reasonable and rapid changes due to the immersion process. Hence, a 1 mm thin sample was used. Further, in the mouth the lining is bonded to the acrylic denture base. Thus displacement is restricted by the bonding and it might be speculated that 1 mm unbonded would be similar to 2 to 3 mm bonded (Wright, 1976). Moreover, for the purposes of standardization, the 1 mm thick specimens were placed on a metal plate during testing. Acrylic resins have an approximate Shore A hardness of 100, compared with metal plate having a Shore A value of 100. Therefore, the conditions were quite similar to the lining being supported by a denture base resin.

6.4.2 Silicone-based denture soft lining materials

Softness is obviously a desirable property for a denture soft lining material. Maintaining compliance as the material ages may increase patient comfort during clinical use. In this study, hardness of the Molloplast-B® and Ufi Gel SC remained essentially constant throughout the experimental period. The initial Shore A hardness values for the silicone-based denture soft lining materials ranged between 23.3 (Ufi Gel SC) and 34.6 (Molloplast-B®). Hardness values for the Molloplast-B® were consistently greater than the Ufi Gel SC. This result was consistent with that reported by Parr and Rueggeberg (2002), who compared an autopolymerised and a laboratory-processed silicone-based denture soft lining material. The main reasons for the difference in hardness appear to be different ingredients, filler loading and curing mode. Increased processing temperatures were expected to result in a more complete polymerisation reaction and thus a stiff polymer network (Odian, 1991).

The silicones displayed varying results on storage, with Molloplast-B® softening slightly and Ufi Gel SC hardening slightly. However, their compliance on storage did not show

any significant statistical change. For silicone-based denture soft lining materials, their compliance is an inherent physical property of the materials.

In this study the effect of food simulating liquids on silicone-based denture soft lining materials did not appear to be clinically significant. This result was consistent with previous reports (Sauer, 1966; Mäkilä, 1976; Wright, 1984; Wright, 1986; Schmidt and Smith, 1983b), which reported the silicone-based denture soft lining materials maintain their softness over a long period of time although these reports were generally based on subjective opinions or clinical surveys.

6.4.3 Methacrylate-based denture soft lining materials

The initial Shore A hardness values for the methacrylate-based denture soft lining materials ranged between 25.6 (EverSoft®) and 53.7 (Vertex™Soft). The main reasons for the differences in hardness appear to be different structures of the materials, ingredients, particle size of the polymer and curing mode. Vertex™Soft liquid contains crosslinkers and crosslinks by heat. This would enhance the material's strength and reduce flexibility.

Loss of compliance in the oral aqueous environment has most often been reported with plasticised acrylic materials (Travaglini *et al.*, 1960; Craig and Gibbons, 1961; Graham *et al.*, 1990; Jepson *et al.*, 1993a) because of the susceptibility of the plasticiser to leaching out of the material. In this study, an increase in hardness was expected resulting from plasticiser and ethanol loss noted from the water/fluid uptake data. However, Shore A hardness values did not reflect significantly the effect of food simulating liquid immersion except in oils (coconut oil and HB307). Although Vertex™Soft and EverSoft® lost 1-13% of their weight when immersed in distilled water after one year, they do not significantly change their compliance. Vertex™Soft overall increases in weight by 3% after one year immersion in distilled water, but the real uptake is 4%. For EverSoft® the comparable figures are 5% and 18%. This illustrates that loss of plasticizers and ethanol are replaced to a great extent by the distilled water. This is different from what is expected from clinical observation. Low molecular weight plasticisers are reported to be far more susceptible to loss from the matrix (Graham *et al.*, 1991) and in-turn this may

facilitate water/fluid absorption. Most likely the low molecular weight plasticisers are not lost totally from the matrix and, in addition, water itself is a weak plasticiser (Suchatlampong *et al.*, 1975; Craig and Gibbons, 1961) which may provide plasticisation and thus, should result in on overall decrease in compliance. Actually with the exception of artificial saliva and oil environments, Vertex™Soft and EverSoft® showed an increase in compliance with time. A decrease in compliance only occurred in oil environments and in artificial saliva corresponding to what would be expected from the considerable loss of substances leading to a final decrease in weight. These suggest that the coconut oil and HB307 facilitate plasticiser-leaching resulting in a decrease in compliance. The lower fluid uptake in artificial saliva was caused by the osmotic pressure factor. The real uptake of artificial saliva is not significantly different from distilled water and the small decreased compliance in not significant.

6.4.4 Experimental bromo-butyl butyl elastomer

The experimental bromo-butyl butyl elastomer failed to show any effects of food simulating liquids except in oils. Hardness shows a similar trend with insignificant change in food simulating liquids, except in oils. This is attributed to its polymer network which appears to be stable in weak acids, artificial saliva, water, and alcoholic drinks. Actually, the bromo-butyl butyl elastomer initially showed a higher hardness value but in oils exhibited the lowest hardness value with time. This uptake study demonstrated plasticisation by oil resulting in swelling, dimensional change, loss of strength and increase in compliance. Thus, the polymer molecular structure and network in oils appears to undergo degradation. This is supported by the visual assessment of the specimens where samples had disintegrated or swollen (Figure 5.38).

6.4.5 Summary

This study has shown that food simulating liquids were associated with change in compliance of denture soft lining materials. The degree of change varied with each generic type of material. The loss of substances leading to final weight changes produces some explanation of hardness changes from the interaction between the food simulating liquids and the denture soft lining materials. Summarily, the three measurements (weight

changes, loss of substances or solubility and Shore A hardness) support one another in suggesting what will happen changing the interaction between food simulating liquids and hardness or compliance.

6.5 The interaction between denture soft lining materials and food simulating liquids: changes in the surface roughness

6.5.1 Validity of the method

Conventional contact stylus profilometers, as used for many engineering applications, have been used for roughness measurement in dental research (Heath and Wilson, 1976; Zissis *et al.*, 2000). The major disadvantage of using a stylus profilometer is underestimation of the roughness and spikiness of the surface due to the deeper surface irregularities being narrower than the stylus itself. Further, the contact stylus may damage the surface, and it may produce an erroneous measurement due to the elastic rebound. A non-contact laser measurement reduces these problems. Conversely, the laser non-contact stylus may produce erroneous measurements because of an overshoot phenomenon as the laser light is reflected from the sub-surface rather than the actual surface. However, the laser stylus is effective with on opaque surface (Whitehouse, 1997).

The surface roughness of a material used for a removable prosthesis is of importance since it affects directly or indirectly plaque accumulation, stain retention, and patient comfort (Bollen *et al.*, 1997; Veres *et al.*, 1990). For conventional heat-cured denture soft lining materials, the specimen preparation procedure resembled the conventional laboratory flasking technique used in clinical practice but for autopolymerised materials, which are used in the mouth for chair-side relining, the same preparation was less realistic. For convenience and infection control, samples could not be prepared intra-orally but were prepared in flasks like the heat-cured materials.

6.5.2 Surface roughness parameters

To describe the surface texture of the denture soft lining materials following immersion in different food simulating liquids, several parameters were selected. Most studies have used an amplitude parameter (R_a) as the only indication of surface texture. However, R_a

can not represent the true surface texture because it averages surfaces with deep and shallow grooves but lacks information on the profile of the irregularity, as peaks or valleys (Whitehead *et al.*, 1996). Other parameters including R_q and R_{max}, which can be equally important, were also measured for peaks, valleys, and profile shape. The more complicated the shape of the surface, the more sophisticated the measuring parameters need to be beyond R_a. For this reason, R_a, R_q and R_{max} were all recorded in this study.

6.5.3 Silicone-based denture soft lining materials

In this study, for the silicone-based materials, R_a values are slightly less then those reported by Zissis *et al.* (2000), whereas the differences found for autopolymerised materials may be because of the application of glazing supplied by the manufacturer as a finishing procedure to smooth out the roughness of the material.

It should be noted that the lowest surface roughness values were found on Ufi Gel SC stored in all liquids for all testing periods. Glazing has been suggested as effective in smoothing the surface by coating over the irregular surface (SPI for Ufi Gel SC, 2000), although it was not the case for Molloplast-B® (Zissis *et al.*, 2000). Since the surface roughness of Ufi Gel SC was unchanged during storage in all liquids for all testing periods it seems likely that the glazing material remained bonded to the surface. This result may also be related to the lack of significant weight changes of Ufi Gel SC in all liquids.

6.5.4 Methacrylate-based denture soft lining materials

After immersion in food simulating liquids, the changes of surface roughness with time were strongly affected by the food simulating liquid. A significantly higher average, root mean square and maximum surface roughness ($P<0.05$) was observed for EverSoft® in all liquids except oils, and Vertex™Soft in 50 per cent ethanol. Generally, this agrees with the finding of Jin *et al.* (2003), who investigated the effect of denture cleansers and distilled water on surface roughness of denture soft lining materials up to 180 days.

The simplest interaction between materials and the immersion liquid is the transfer of material across the material-liquid interface in the absence of a reaction. Inherently, if the fluid moves into the material, the result will be swelling. However, the structure will not swell uniformly which may cause a difference of surface roughness. Further, when the soluble component of the material, such as the plasticiser, dissolves in the storage solution, the resulting material porosity is said to be due to leaching (Lee *et al.*, 1998). Both of these effects have profound influences on the behaviour of materials despite the absence of externally applied stress and obvious shape changes. As previously described, the storage solvent penetrates the polymer network molecular structure and expands the opening between polymer chains, so plasticiser may diffuse out leaving empty spaces, surface voids or bubbles. Probably with time, these surface voids or bubbles, responsible for the roughness, increased in size resulting in craters. The crater boundaries probably diminish when compared with those of the bubbles and the specimens become smooth. On the contrary, when EverSoft® and Vertex™Soft were immersed in oils for the same periods of time, shrinkage and leaching both resulted from the process of diffusion. The empty space or bubbles may be filled or coated with remaining oils, resulting in low roughness values. The shrinkage may also be contributory to lower roughness values.

However, it is important to consider the role of EverSoft® sealer on the surface. In this study, the lowest surface roughness values were also found on EverSoft® stored in distilled water, artificial saliva, 3 per cent acetic acid, 10 per cent ethanol and 50 per cent ethanol for the initial stages (less or equal 1 day). Sealing has been suggested as effective in smoothing the surface (MSDS for EverSoft®, 2004). Since the surface roughness and weight changes of EverSoft® changed with time in all liquids it seemed likely that the sealer material did not chemically bond to the intact surface. Thus, in this study the application of sealer only smoothed the surface of EverSoft® for the initial stages.

6.5.5 Summary and clinical implications

It is generally acknowledged that plaque and other biological materials accumulate more easily on a rough surface than a smooth surface (Guevara *et al.*, 1977). Since a roughened surface attracts plaque, there should be a threshold below which no further reduction in

microbial accumulation can be expected. Bollen *et al.* (1997) have suggested a "threshold of R_a value" located at a score of 0.2 μm. According to the finding of this study, no material tested was found to achieve this level of smoothness, although some exhibited low Ra values ranging from 0.3 to 0.8 μm, for example, coconut oil on the surface of Ufi Gel SC or EverSoft®. Higher surface roughness could increase the possibility of microbial colonization, which can dramatically decrease the life of denture soft lining materials. The roughness could also aggravate tissue abrasion. However, it is not known what effect abrasion of the surface due to function and cleaning might have.

In this study, the methacrylate-based denture soft lining materials exhibited an increase in surface roughness after immersion in food simulating liquids except in oils. Oil application as a post-treatment maintains the roughness in comparison to other food simulating liquids. Moreover, there was no statistically significant change found in the surface roughness following immersion of silicone-based denture soft lining materials in food simulating liquids.

6.6 The interaction between denture soft lining materials and food simulating liquids: wettability properties

6.6.1 Validity of the method

Saliva plays an important role in the retention of removable prostheses. To maintain sufficient denture adhesion to the local denture bearing mucosa, saliva must wet the surface of the denture and flow easily over the tissue surfaces of the denture (Niedermeier and Krämer, 1992). However, denture soft lining materials are not only coated by saliva but also contaminated by ingested food, liquids and oral fluids which may provide an adequate lubricating film between the lining and the supporting tissue to achieve better retention and prevent frictional problems. The retention of a denture thus relies on the wettability properties between the medium (saliva or oral fluids) and the denture soft lining materials. The use of artificial saliva and other food simulating liquids in this investigation introduce clinically relevant conditions and it was considered that the equilibrium contact angles between water or food simulating liquids and various denture soft lining materials would give a useful comparative assessment.

The wettability of a solid by a liquid is determined by measuring the contact angle between a drop of the liquid and the plane surface of the solid. In this study, the static sessile drop technique (optical method) was used to measure the contact angle. This is a quick and convenient method of comparing contact angles for denture soft lining materials.

6.6.2 Control of variables

Wettability is affected by surface chemical properties, such as polarity, surface tension and contact angle, together with the influence of contamination on the surface of the material. To reduce the chance of contamination, care was taken not to touch the surfaces of specimens except with metal tweezers. Each specimen was placed on a metal stage to maintain it horizontal. Good lighting is important for a good image, and care was taken to ensure lighting from various angles on the stage to avoid shadow. The drop volume can decrease due to evaporation and this was avoided by measuring within 15 seconds of the droplet spreading on the surface.

The equilibrium contact angles recorded for all of the denture soft lining materials were comparable with those found by other researchers (Wright, 1980a; Waters *et al.*, 1995). Unfortunately, in almost every case the conditions of testing were not adequately defined or were different so that direct comparisons cannot be made. Moreover, reports of the wettability of denture soft lining materials are relatively limited. Hence, as previously stated, the purpose of this investigation was to test the denture soft lining materials as they are used clinically.

6.6.3 Silicone-based denture soft lining materials

Generally, poly(dimethylsiloxanes) are low surface energy solids exhibiting poor wettability and, thus, a large increase in surface energy would be needed to achieve adequate lubrication and minimize irritation of the mucosa (Polyzois *et al.*, 1991). In this study, the findings failed to show consistent significant differences in the equilibrium contact angle between the silicone-based denture soft lining materials after immersion in the majority of the food simulating liquids tested. Molloplast-B® still exhibited a high

equilibrium contact angle with distilled water, artificial saliva, 3 per cent acetic acid, 10 per cent ethanol and 50 per cent ethanol after one year immersion. The results are in general agreement with Waters *et al.* (1995). Ufi Gel SC also showed low wettability. However, the equilibrium angles of water on Molloplast-B® and Ufi Gel SC after immersion in coconut oil and HB307 significantly decreased with time when compared to the equilibrium contact angles for water on Molloplast-B® and Ufi Gel SC in other liquids. Immersion in oils showed improved wettability compared to immersion in other food simulating liquids.

It is most likely that the oils caused the surface tension between the materials and the water to weaken. In general, for a substance to reduce surface tension of water (72 dynes/cm) the substance must be "surface active". This means that it has a hydrophobic end and a hydrophilic end which is particularly effective in reducing the surface tension of water (Craig and Powers, 2002). The surface tension may already be significantly lower than that of pure water because of the presence of components like coconut oil which certainly would be a candidate surface active agent. This kind of wetting agent may be incorporated with detergents to lower the surface tension, making the solution or water wet better. The attraction between the water molecules has been reduced by merely interspersing molecules of detergent between them. This reduces the tension or attraction, not only at the surface but also throughout the solution. Ferraz *et al.* (2002) confirmed their crude precipitate surfactant included coconut oil which reduced the surface tension of water from 72 to 28.7 dyne/cm.

The improvement in wettability appears to be due to the remaining oil on the surface as an intermediate layer between the water and the solid surface. This leads to a much lower interfacial tension against water due to the hydrogen bonding capability and high dipolar moment of the water molecule. As these molecules occupy surface positions in the distilled water-air surface, they displace surface water molecules, thus reducing the cohesive force in the distilled water. The phenomenon is very similar to the function of surface active agents (Craig and Powers, 2002). The presence of the long-chain fatty acid molecules in the surface layer reduces the pull of the surface molecules on the liquid mass. This reduces the surface tension thus increasing wetting.

6.6.4 Methacrylate-based denture soft lining materials

The initial equilibrium contact angles for the methacrylate-based denture soft lining materials ranged between 73.0 and 80.7. The results are in general agreement with previous work (Wright, 1980a; Waters *et al.*, 1995) in respect to the methacrylate-based denture soft lining materials showing greater wettability than the silicone-based denture soft lining materials, when contact angles ranged from 86.1 to 93.3. The surface energy of the former is larger than the latter (Waters *et al.*, 1995). In this study, the finding that the equilibrium contact angle measurement of the auto-polymerising EverSoft® was similar to the heat-polymerising Vertex™Soft is also in agreement with the report of Zissis *et al.* (2001). This result may be explained by their similar surface structure leading to similar surface energy. As previously described, oils would be a candidate surface active agent to reduce the surface tension of water. This is why the equilibrium angles of Vertex™Soft and EverSoft® after immersion in coconut oil and HB307 were significantly decreased with time when compared to the equilibrium contact angle in other liquids. Overall, oils were successful at improving wettability. The adaptation of oil as a successful wetting agent for denture soft lining materials to improve wettability and maintain their dimensional stability and compliance will be an interesting task for the future.

6.6.5 Experimental bromo-butyl butyl elastomer

Little change was observed with time in distilled water, artificial saliva, 3 per cent acetic acid, 10 per cent ethanol and 50 per cent ethanol and it seems to be stable in these environments. This is due to the polymer molecular network stability in weak acid, alcohol drinks and water. Immersion in oils produces a significant difference, and this is a major problem when compared to the other liquids. For bromo-butyl butyl elastomer, oils are not only a candidate for a surface active agent to reduce the surface tension of water, but their long-chain fatty acid molecules can penetrate even well-packed surfaces, which causes swelling and the polymer molecular network to undergo fast decomposition. The fluid uptakes in oils were unacceptably high for clinical usage. Fluid absorption into the material will result in dimensional change, which will lead to stress at the liner/denture base interface and reduce bond strength. Thus, any increase in fluid absorption through

the use of such a surface wetting agent would be detrimental to the clinical use of the material.

6.6.6 Summary and clinical implications

The present study measured the wettability of four commercial denture soft lining materials and one experimental elastomer, showing that, in general, silicone-based denture soft lining materials exhibit a greater equilibrium contact angle than methacrylate-based denture soft lining materials and bromo-butyl butyl elastomer, which may lead to reduction in saliva lubrication when in contact with the oral mucosa. Oil immersion as a coating improves the surface wettability in comparison to other food simulating liquids. However, this treatment would not be suitable for bromo-butyl butyl elastomer.

6.7 The interaction between denture soft lining materials and food simulating liquids: Candida albicans adherence

Candida albicans is a common aetiological agent in denture-related stomatitis (Budtz-Jørgensen, 1974; Mäkilä and Hopsu-Hava, 1977). Denture soft lining materials alone do not support yeast growth but it has been suggested that accumulated debris in the pores of the material can support yeast growth (Wright *et al.*, 1998). Surface irregularity, the type and degree of roughness of the surface are believed to be contributory (Verran *et al.*, 1991). Another contributory factor in the aetiology of denture-related stomatitis is trauma from ill-fitting dentures. Although denture soft lining materials can help to prevent trauma from the denture, insufficient lubrication by saliva may cause frictional trauma. A reduction in *Candidal* colonisation combined with increased lubrication between the denture surface and oral mucosa would presumably decrease this risk. Thus, the reasons for choosing coconut oil as a treatment option is as follows: firstly, coconut oil is a natural oil and no adverse effects have been demonstrated (Agero and Verallo-Rowell, 2004; Sankaranarayanan *et al.*, 2005) which may also explain why the FDA chooses HB307 and Miglysol™812 (both are derived from coconut oil) to represent fatty foods. Secondly, coconut oil might be suitable as a wetting agent and lubricant to reduce

abrasion between the degenerative oral mucosa and the hard denture base (Ferraz *et al.*, 2002).

In this study, the use of various coating agents on the adherence of *Candida albicans* showed interesting results. They exhibited clear differences between the oil-treated and no treatment denture soft lining materials, with the oil-treatment surface showing a significantly reduced colonisation by *Candida albicans*. Bergsson *et al.* (2001) have reported that two medium-chain fatty acids (lauric acid and capric acid) were active in killing *Candida albicans*. Both lauric acid (47.1 per cent) and capric acid (7.5 per cent) are components of coconut oil. Thus, the coconut oil may be active in reducing the *Candida albicans* adhesion and have a direct antifungal activity. Moreover, previous studies have indicated that the hydrophobicity and surface energy of a biomaterial can affect microbial adhesion (Everaert *et al.*, 1998; Miyake *et al.*, 1986). This study speculates that a coating of coconut oil successfully changed the hydrophobic function of silicone surfaces. This was indicated by the decrease in the equilibrium water contact angle (see section 6.6).

The effect of a sealer could be to seal the pores in the denture soft lining material, prohibiting entry of *Candida albicans* into the body of the material. As previously discussed, the sealer would fill surface irregularities. Is a sealer a physical barrier? Sealants have been developed to smooth the surface and control surface contamination with stain or bacteria (SPI for Ufi Gel SC, 2000; MSDS for EverSoft®, 2004). However, it should be noted that Ufi Gel SC sealer is a silicone-based material and could bond chemically with Ufi Gel SC and Molloplast-B® but only bond mechanically with Vertex™Soft and EverSoft®. Moreover, the sealer of EverSoft® does not chemically bond to the surface of Ufi Gel SC, Molloplast-B®, Vertex™Soft and EverSoft® due to a different structure. The inhibition of *Candida albicans* adhesion by the sealer could be the result of a decrease in surface roughness. However, the sealer also changes the surface energy characterisation, and this could increase *Candida albicans* adhesion. In this study, the results were in agreement with the report of Lefebvre and Schuster (2002), which reported no difference between specimens with a smooth or irregular surface or

those treated with sealant and without. Thus, they suggested *Candida albicans* is able to adhere to the surface of PermaSoft® denture soft lining material regardless of surface texture or use of sealant.

In summary, this investigation found that the use of a glazing material plus coconut oil on denture soft lining materials, especially the silicone-based denture soft lining materials, may be a beneficial adjunct. Specimens of denture soft lining materials treated with glazer plus coconut oil showed significantly less *Candida albicans* adhesion than only oil treatment, no treatment and only sealer treatment. Further research is needed to determine the mechanism of *Candida albicans* inhibition by coconut oil, as well as the longevity of the beneficial effects. The practical consideration of the patient applying the oil, are also related to the longevity of the effect. Moreover, a correlation between surface energy, surface roughness and adhesion would be an interesting interaction to investigate.

6.8 The interaction between denture soft lining materials and food simulating liquids: leachable substance detection

This work was carried out using FTIR. To ensure an accurate reading, the diamond crystal head and all surrounding areas were cleaned with acetone before and after each process. The test failed to show any obvious leachable substances from any of the denture soft lining materials stored in all liquids for up to one year. This may have been because the concentration of the leachable substance was too low to be detectable in the 50 ml of immersing solutions, or these findings could suggest that the leachable substances were susceptible to chemical breakdown in all liquids. A minimum of 10% of material in solution is normally required to be detected. This concentration may not have been reached in the volume of immersing fluid. It appeared that there was insufficient material leached out of the test material to produce a significant result. An alternative more sensitive method using HPLC (high-pressure liquid chromatography) could be considered in future investigation.

CHAPTER SEVEN

CONCLUSIONS AND FUTURE WORK

7.1 Conclusions

The results of this study showed that long-term storage of denture soft lining materials in different food simulating liquids affected the properties of the materials differently according to their generic type. The methacrylate-based denture soft lining materials took up as much as 7% of water whereas the silicone-based and the experimental elastomer absorbed 2% and 10% of water, respectively, when they were immersed in distilled water. The changes were more pronounced when the materials were stored in the other six food simulating liquids.

Methacrylate-based denture soft lining materials were more susceptible to degradation, where plasticiser loss appears to be influenced by osmotic gradients, oil solubility and concentration. Silicone-based denture soft lining materials were not affected by storage in food simulating liquids. Bromo-butyl butyl elastomer absorbs oil components in the range 174-215% followed by a loss of strength and decrease in hardness.

The methacrylate-based denture soft lining materials, in regularly changed 50 per cent ethanol, coconut oil and HB307 showed degradation similar to that seen during intra-oral use. The changed 50 per cent ethanol might be the most suitable solvent presently available to simulate oral fluids because it most closely reproduces changes which have been observed for soft linings in clinical use.

The Shore A hardness of silicone-based denture soft lining materials was not affected by storage either in distilled water or food simulating liquids. However, for other materials, different food simulating liquids had variable effects with food oils being the most likely cause of rapid degradation of one experimental elastomer and two plasticised methacrylate materials. Shore A hardness evaluation confirmed the uptake results.

The methacrylate-based denture soft lining materials generally exhibited an increase in surface roughness after immersion in food simulating liquids.

In general, silicone-based denture soft lining materials exhibit a greater equilibrium contact angle in comparison to methacrylate-based denture soft lining materials and bromo-butyl butyl elastomer. Oil immersion as a post-treatment improves the surface wettability in comparison to other food simulating liquids. However, this treatment would not be suitable for the bromo-butyl butyl elastomer.

In this study, the use of a sealer plus coconut oil on denture soft lining materials especially silicone-based denture soft lining materials, showed significantly less *Candida albicans* adhesion than only oil treatment, no treatment, only sealer treatment.

Different food simulating liquids have variable effects with food oils and changed 50% ethanol being the most likely cause of rapid degradation of the methacrylate-based denture soft lining materials. Thus, the different behaviour on immersion in food simulating liquids should be taken into consideration when testing materials, since the results are more likely to be clinically relevant than those for distilled water.

7.2 Future work

Denture soft lining materials are used in the clinical situation bonded to PMMA. The effect of bonding of one surface on fluid uptake in food simulating liquids is unknown. Specimens could be designed to investigate this. Moreover, tests could also be carried out using thermocycling as this may be more clinically relevant.

The effect of the bonding between denture soft lining materials and the hard denture base materials on dimensional changes as a result of fluid imbibition would also be interesting.

Abrasion resistance of the denture soft lining materials could be assessed and the effect of abrasion on surface roughness. Further the effect of denture cleansers on surface roughness should be investigated.

The properties of the silicone-based materials would seem to be related to the inorganic (hydrophobic) filler used in their composition. Further analysis of these fillers is indicated both in terms of the actual filler used and the bonding mechanism between the filler and the silicone rubber. Additionally, for the commercial denture soft lining materials and the experimental elastomer the degree of cross-linking would seem to merit further investigation.

The storage medium should be analysed using HPLC to determine the soluble species leached out from the denture soft lining materials. Any leached constituents from these materials needs to be evaluated together with the rate at which they leach.

Further research is needed to determine the mechanism of *Candida albicans* inhibition by coconut oil, as well as the longevity of the beneficial effects. Moreover, a correlation between surface energy, surface roughness and adhesion would be an interesting interaction to investigate.

Finally despite extensive investigation, this study has been unable to simulate many of the detrimental changes found during normal clinical use, especially in respect of the silicone-based materials. This remains the ultimate aim.

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APPENDIX

A.1. Diffusion theory and Fick's laws

Diffusion in polymers essentially originates from the classical equations of Adolf Fick. In 1855, Fick recognised the basic similarity between two processes, namely, diffusion and heat transfer by conduction, and proposed the laws of diffusion in analogy with the theory of heat conductivity. Crank (1975) defined the diffusion as "*the process by which matter is transported from part of the system to another as a result of random molecular motions*".

Diffusion of water is a time-dependent process where water is transported from the environment through the material surface into its bulk as a function of time (Callister, 2003). The mathematical theory of diffusion in isotropic substances is based on the hypothesis proposed by Fick's continuum theory.

Describes the rate of transfer of diffusing substance or flux through a unit area of a section as proportional to the concentration gradient measured normal to the section. The rate by which matter diffuses is measured by the diffusion coefficient.

Equation I.1

$$F = -D\frac{\partial c}{\partial x}$$

Where;

F = the rate of transfer per unit area of section (flux),

c = the concentration gradient of diffusing substance,

x = the space co-ordinate measured normal to the section (thickness), and

D = the diffusion coefficient.

If the rate of diffusion does not change with time, the condition is known as "steady-state diffusion" (Callister, 2003). This occurs when the concentrations of the diffusing species on both surfaces of the section are held constant. In mathematics in steady-state diffusion, the rate of diffusion is proportional to the concentration gradient. This permits the

calculation of a diffusion coefficient (***D***) with the unit of length^2 time^{-1} or cm^2 sec^{-1}. The negative sign in this equation indicates that the diffusing species moves in the opposite direction of increasing concentrations.

However, most diffusion processes are "non steady-state"; the rate of diffusion and the concentration gradient vary with time. Non steady-state diffusion also occurs in a non-homogeneous media where the diffusion coefficient varies from point to point (Callister, 2003). For these conditions, "Fick's second law" addressed this.

By considering the mass balance of an element of volume, provided that D is a constant, the fundamental differential equation of diffusion is better expressed in the form;

Equation I.2

$$\frac{\partial c}{\partial t} = D\left(\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} + \frac{\partial^2 c}{\partial z^2}\right)$$

However, in many polymer systems, D depends markedly on the concentration, c. When the medium is not homogeneous (thus D varies from point to point), equation I.2 becomes;

Equation I.3

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial c}{\partial x}\right) + \frac{\partial}{\partial y}\left(D\frac{\partial c}{\partial y}\right) + \frac{\partial}{\partial z}\left(D\frac{\partial c}{\partial z}\right)$$

Where D may be a function of x, y, z and c. Most commonly, diffusion occurs effectively in one direction only (i.e. there is a gradient of concentration only along the x-axis), thus equation I.2 and equation I.3 then becomes;

Equation I.4

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}, \text{ and}$$

Equation I.5

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial c}{\partial x}\right), \text{ respectively.}$$

It is often assumed that the diffusion coefficient is constant to simplify the complex diffusion, however this is seldom the case.

In a non-homogeneous medium the diffusion coefficient is concentration dependent and Fick derived a mathematic relationship accounting for this by assuming different concentrations at different points within the structure of the materials. Thus, by measuring the uptake of species for a long time by the material, it is possible to calculate the diffusion coefficient according to *Equation I.6*.

Equation I.6

$$\frac{M_t}{M_\infty} = 2\sqrt{\frac{Dt}{\pi l^2}}$$

Where $2l$ is the thickness of thin plane sheet, M_t is the weight gain after time t and M_∞ is the final weight gain after an infinite time or at equilibrium, Dt is diffusion coefficient at time t.

Various solutions to Fick's second law allow development of a relationship between the concentration of diffusing species for specific geometries and boundary conditions. Derivations of Fick's laws can be used to describe the early line region of water uptake and allows the diffusion coefficient to be determined.

Fickian diffusion is controlled by a concentration-dependent diffusion coefficient, *i.e.* the diffusion coefficient increases as the concentration of diffusing species increases, but does not depend on any other factors. The representative plots for the Fickian and non-Fickian diffusion are given in Figure A.1.

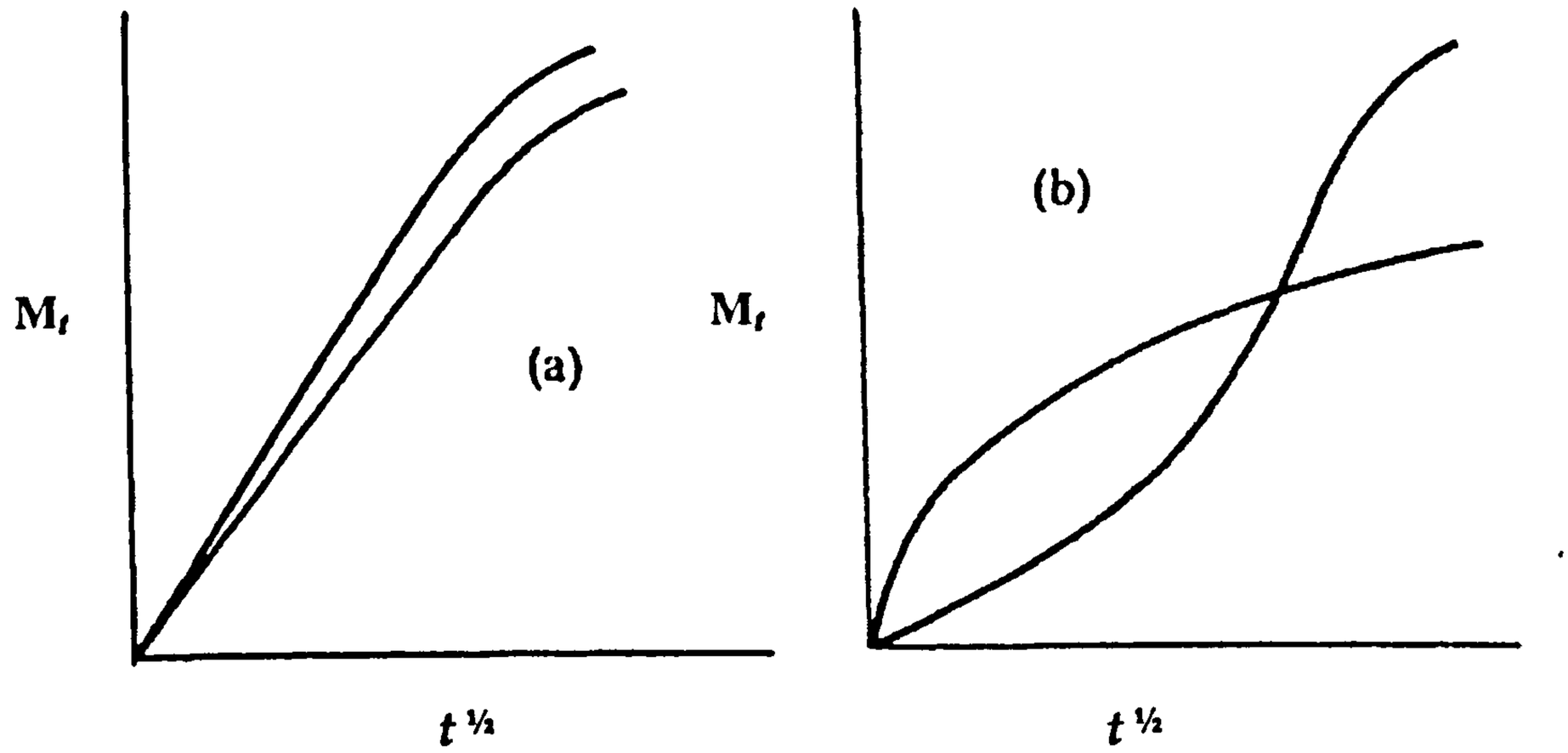

Figure A.1 Fickian-type sorption and desorption curves compared with 'Non-Fickian' or 'anomalous' curve (adapted from Crank, 1975).

In the early stages of Fickian diffusion, the amount absorbed or desorbed is directly related to the square root of time, $t^{1/2}$. The line sorption or desorption curve may extend well beyond 50% of the final equilibrium uptake or loss.

The diffusion behaviour of some polymers, such as glassy polymers, cannot be described adequately by a concentration-dependent form of Fick's law with constant boundary conditions, particularly when the diffusing species causes extensive swelling of the polymer (Crank, 1975). The properties of these polymers are time-dependent, i.e. they respond slowly to the changes in their conditions. As a result, their behaviour deviates from that of Fick's law due to the slow rate of response to the sorption or desorption of diffusing molecules and the curve has no initial linear portion (Figure A.1b). Therefore, diffusion can be classified into three classes based on the relative rates of penetrant diffusion and relaxation of the polymer (Crank, 1975; Lasky *et al.*, 1988).

Case I diffusion, or Fickian diffusion, occurs when the rate of diffusion is significantly slower than the rate of relaxation of the polymer chains. Uptake increases linearly when plotted against $t^{1/2}$ in the initial stages before equilibrating.

Case II diffusion occurs when the rate of penetrant diffusion is greater than the rate of relaxation of the polymer chains.

Case III, or anomalous diffusion, occurs in the transition region between case I and case II, when the rates of penetrant diffusion and polymer relaxation are comparable.

The mechanisms of the transport of solvents into polymers may be determined by a variety of experimental techniques, the simplest and most common of which is the sorption technique. In a sorption experiment, including both absorption and desorption of a penetrant, the gain or loss in the mass of the polymer, M_t, is monitored as a function of square root of time, $t^{1/2}$.

A.2 Hardness and related matters on soft lining materials

It has long been known that there is a relationship between the Shore and International Hardness on the one hand, and the Young's Modulus on the other. Gent (1958) showed that this relationship could be explained from the classical elasticity theory of the deformation of indenters, first derived by Hertz. In the case of a cylindrical indenter, to which the Shore instrument approximates (Gent, 1958):

Equation II.1

$$d = \frac{F(1-\nu^2)}{2RE}$$

Where d is the depth of indentation under a force F; R is the radius of the indenter, E the Young's Modulus of the test material, and ν the Poisson's ratio of the test material. As elastomers are incompressible, $\nu = 0.5$, so equation *II.1*) can be rewritten:

Equation II.2

$$d = \frac{3F}{8RE}$$

On this basis Gent (1958) derived the following* equation for the relationship between Young's Modulus (E) and Shore Hardness(s):

Equation II.3

$$E(MPa) = \frac{9.81(56+7.66s)}{[2.67R(254-2.54s)]}$$

* Gent's formula has been modified to give E in SI units.

For this reason ASTM D2240-86 specifies that a specimen must be at least 6mm thick, and that the lateral dimensions shall be sufficient to permit measurements at least 12mm from any edge. It further states that a specimen may be composed of plied pieces to obtain the necessary thickness, *but determinations made on such specimens may not agree with those made on solid specimens, because the surfaces between plies may not be in complete contact.* It should be added that the nature of the stress distribution at such interfaces is also an unknown factor.

Waters (1965) has studied the load indentation characteristics of rubber sheets by cylindrical indenters as a function of specimen thickness, for thicknesses in the range 1.5 to 18mm using vulcanised rubbers with a range of Moduli values of ~0.82-4.12 MPa. Two cases were studied i.e where the bottom surface was unlubricated and lubricated respectively. It was found that the data could be represented by the following modification to *Equation II.4*):

Equation II.4

$$d = \frac{3F}{8RE.\phi(t/R)}$$

where t is the thickness of sheet, and $\phi(t/R)$ is a universal function, modifying the Hertz equation for thin specimens. The relationship between the movements of the indenter d is related to the hardness reading by Gent (1958) and Waters (1965)

Equation II.5

$$d\,(cm) = 0.254 - 2.54.10^{-3}s$$

The formula for converting the Apparent Hardness (Ha) to the ASTM Shore Hardness (H) is:

Equation II.6

$$H = \frac{[H_a - 39.9]}{0.61}$$

A.3 Surface Roughness Tables

The roughness parameters obtained from laser profilometer of denture soft lining materials as processed and following immersion in seven food simulating liquids are presented in Tables A.3.1-7.

Table A.3.1 Summary of R_a, R_q and R_{max} (μm) of denture soft lining materials following immersion in distilled water (DW) at 37±1°C at various time intervals, mean ± sd

R_a (DW)	**Material**			
Test period	**Vertex™Soft**	**EverSoft®**	**Molloplast-B®**	**Ufi Gel SC**
baseline	1.96 ± 0.45	0.71 ± 0.32	2.04 ± 0.84	0.42 ± 0.02
1H	2.43 ± 0.83	0.63 ± 0.30	4.02 ± 1.89	0.34 ± 0.02
1D	2.47 ± 1.11	1.28 ± 0.69	1.79 ± 0.73	0.22 ± 0.04
1W	2.35 ± 0.26	5.41 ± 3.42	2.96 ± 1.28	0.36 ± 0.15
1M	2.23 ± 0.40	6.11 ± 0.84	2.88 ± 0.75	0.83 ± 0.44
1Y	6.02 ± 3.64	10.42 ± 1.64	4.76 ± 2.55	0.61 ± 0.31
R_q (DW)				
baseline	3.03 ± 0.88	1.24 ± 0.64	3.18 ± 1.58	0.59 ± 0.02
1H	4.03 ± 1.70	0.89 ± 0.42	8.02 ± 5.35	0.47 ± 0.03
1D	3.67 ± 1.84	2.46 ± 1.56	2.77 ± 1.19	0.30 ± 0.04
1W	3.73 ± 0.36	9.92 ± 6.41	4.99 ± 2.99	1.04 ± 0.70
1M	3.47 ± 0.84	11.14 ± 1.50	4.32 ± 1.62	1.78 ± 1.14
1Y	10.16 ± 6.68	17.15 ± 1.02	9.57 ± 5.50	1.23 ± 0.84
R_{max} (DW)				
baseline	24.07 ± 7.36	8.62 ± 6.62	25.41 ± 14.77	5.43 ± 1.54
1H	35.76 ± 18.21	5.67 ± 3.85	58.41 ± 41.76	4.28 ± 0.23
1D	33.56 ± 14.76	14.38 ± 15.88	25.03 ± 11.51	3.84 ± 1.01
1W	30.95 ± 4.28	47.14 ± 39.86	46.89 ± 37.40	16.46 ± 13.35
1M	28.65 ± 9.12	75.28 ± 7.94	34.77 ± 8.44	18.23 ± 7.54
1Y	51.25 ± 12.68	134.64 ± 62.29	81.04 ± 38.81	13.25 ± 8.51

Table A.3.2 Summary of R_a, R_q and R_{max} (μm) of denture soft lining materials following immersion in artificial saliva (AS) at 37±1°C at various time intervals, mean ± sd

R_a (AS)	**Material**			
Test period	**Vertex™Soft**	**EverSoft®**	**Molloplast-B®**	**Ufi Gel SC**
baseline	2.59 ± 1.02	0.62 ± 0.52	2.02 ± 1.11	0.46 ± 0.11
1H	2.99 ± 0.55	0.44 ± 0.14	3.51 ± 1.69	0.55 ± 0.17
1D	2.98 ± 0.81	0.91 ± 0.25	3.47 ± 2.52	0.42 ± 0.09
1W	2.71 ± 1.38	3.47 ± 0.11	3.44 ± 0.47	0.39 ± 0.19
1M	2.24 ± 0.80	4.74 ± 0.82	2.82 ± 2.11	0.63 ± 0.24
1Y	2.59 ± 1.14	5.73 ± 1.43	2.23 ± 0.62	0.50 ± 0.20
R_q (AS)				
baseline	3.97 ± 1.63	1.95 ± 1.28	3.84 ± 3.05	0.79 ± 0.28
1H	5.09 ± 0.61	0.71 ± 0.18	5.94 ± 3.24	0.86 ± 0.21
1D	5.20 ± 2.15	1.91 ± 0.01	6.23 ± 5.87	0.64 ± 0.16
1W	4.09 ± 2.03	7.24 ± 1.16	6.26 ± 1.80	0.64 ± 0.28
1M	3.40 ± 0.96	8.61 ± 1.42	4.57 ± 3.90	1.05 ± 0.35
1Y	4.29 ± 2.19	9.36 ± 2.12	3.83 ± 1.57	0.76 ± 0.32
R_{max} (AS)				
baseline	29.68 ± 10.61	13.63 ± 13.55	39.11 ± 26.98	8.34 ± 3.97
1H	40.80 ± 6.20	6.32 ± 1.55	57.35 ± 41.42	7.49 ± 1.55
1D	40.27 ± 16.61	22.39 ± 3.73	54.98 ± 61.98	5.94 ± 1.42
1W	34.09 ± 16.81	54.28 ± 13.71	51.16 ± 18.35	6.70 ± 1.63
1M	28.09 ± 5.47	86.02 ± 24.53	45.72 ± 49.76	11.17 ± 4.87
1Y	35.82 ± 15.34	67.77 ± 9.90	33.67 ± 17.69	7.85 ± 3.09

Table A.3.3 Summary of R_a, R_q and R_{max} (μm) of denture soft lining materials following immersion in 3% acetic acid (3AA) at 37±1°C at various time intervals, mean ± sd

R_a (3AA)	**Material**			
Test period	**Vertex™Soft**	**EverSoft®**	**Molloplast-B®**	**Ufi Gel SC**
baseline	2.58 ± 1.68	0.86 ± 0.89	1.84 ± 0.77	1.75 ± 0.19
1H	1.95 ± 0.25	1.39 ± 0.19	2.10 ± 0.86	1.11 ± 0.30
1D	2.31 ± 0.45	1.62 ± 0.16	2.39 ± 1.07	1.12 ± 0.36
1W	2.36 ± 0.25	3.59 ± 0.82	1.64 ± 0.13	0.96 ± 0.35
1M	3.60 ± 0.61	8.28 ± 0.26	2.48 ± 0.29	0.84 ± 0.56
1Y	5.80 ± 1.26	14.96 ± 3.30	2.97 ± 1.58	1.42 ± 1.19
R_q (3AA)				
baseline	4.48 ± 3.63	2.42 ± 1.67	3.28 ± 2.07	2.32 ±0.11
1H	3.04 ± 0.60	2.76 ± 0.86	3.67 ± 2.55	1.51 ± 0.46
1D	3.84 ± 0.80	3.12 ± 0.80	3.62 ± 1.93	1.69 ± 0.88
1W	3.93 ± 1.18	7.46 ± 0.03	2.33 ± 0.28	1.55 ± 0.90
1M	6.19 ± 1.95	13.35 ± 2.36	3.80 ± 0.50	2.44 ± 2.57
1Y	8.08 ± 1.87	24.88 ± 3.87	6.58 ± 5.22	3.08 ± 3.33
R_{max} (3AA)				
baseline	39.76 ± 30.58	19.84 ± 13.04	38.43 ± 33.30	13.10 ± 3.11
1H	27.67 ± 6.24	25.76 ± 10.86	33.39 ± 24.27	8.52 ± 2.44
1D	32.47 ± 5.27	24.14 ± 5.45	27.83 ± 15.77	14.18 ± 10.08
1W	33.44 ± 15.42	68.16 ± 7.49	21.48 ± 7.72	16.12 ± 8.82
1M	51.35 ± 22.30	95.74 ± 20.01	33.08 ± 6.41	10.87 ± 12.98
1Y	54.79 ± 15.57	139.55 ± 3.79	73.08 ± 62.57	39.41 ± 47.55

Table A.3.4 Summary of R_a, R_q and R_{max} (μm) of denture soft lining materials following immersion in 10% ethanol (10E) at 37±1°C at various time intervals, mean ± sd

R_a (10E)	**Material**			
Test period	**Vertex™Soft**	**EverSoft®**	**Molloplast-B®**	**Ufi Gel SC**
baseline	2.37 ± 1.22	0.92 ± 0.44	1.15 ± 0.29	0.54 ± 0.01
1H	1.81 ± 0.65	0.70 ± 0.43	2.06 ± 2.04	0.30 ± 0.04
1D	1.68 ± 0.52	2.94 ± 0.90	2.42 ± 1.86	0.40 ± 0.10
1W	2.09 ± 0.93	5.58 ± 1.08	2.00 ± 0.74	0.38 ± 0.06
1M	3.25 ± 1.12	6.91 ± 2.42	3.77 ± 1.67	1.13 ± 1.00
1Y	3.99 ± 3.02	12.55 ± 2.17	2.23 ± 0.77	0.64 ± 0.50
R_q (10E)				
baseline	4.45 ± 2.81	1.70 ± 0.65	2.79 ± 0.93	0.84 ± 0.06
1H	3.13 ± 1.40	1.45 ± 0.63	5.02 ± 6.56	0.42 ± 0.03
1D	2.17 ± 0.67	4.28 ± 0.67	6.17 ± 5.63	0.83 ± 0.68
1W	2.29 ± 0.93	10.38 ± 2.01	4.05 ± 1.53	0.73 ± 0.46
1M	4.70 ± 1.60	10.84 ± 7.13	8.86 ± 3.64	0.65 ± 0.06
1Y	7.33 ± 6.56	16.65 ± 2.77	4.41 ± 0.70	0.71 ± 0.07
R_{max} (10E)				
baseline	40.22 ± 27.25	10.31 ± 3.24	31.47 ± 2.61	10.49 ± 0.63
1H	28.14 ± 14.32	11.31 ± 5.11	48.27 ± 63.31	4.70 ± 1.24
1D	12.96 ± 8.71	35.21 ± 0.91	68.69 ± 65.62	9.37 ± 8.27
1W	14.19 ± 11.95	76.49 ± 2.29	35.27 ± 9.54	8.78 ± 5.32
1M	37.22 ± 12.16	85.98 ± 25.22	68.80 ± 23.01	7.14 ± 2.93
1Y	56.23 ± 47.51	93.01 ± 62.47	45.56 ± 13.54	10.70 ± 3.55

Table A.3.5 Summary of R_a, R_q and R_{max} (μm) of denture soft lining materials following immersion in 50% ethanol (50E) at 37±1°C at various time intervals, mean ± sd

R_a (50E)	Material			
Test period	**Vertex™Soft**	**EverSoft®**	**Molloplast-B®**	**Ufi Gel SC**
baseline	1.67 ± 0.88	1.19 ± 0.74	1.59 ± 0.55	1.11 ± 0.60
1H	1.51 ± 0.73	0.89 ± 0.78	1.65 ± 0.36	0.45 ± 0.19
1D	2.16 ± 0.98	0.92 ± 0.24	1.21 ± 0.33	0.40 ± 0.10
1W	1.70 ± 0.95	1.96 ± 0.89	1.31 ± 0.15	0.38 ± 0.06
1M	1.63 ± 0.75	3.06 ± 2.03	3.03 ± 2.64	1.13 ± 1.00
1Y	7.09 ± 4.07	15.16 ± 3.37	1.46 ± 0.10	0.64 ± 0.50
R_q (50E)				
baseline	2.58 ± 1.46	2.36 ± 1.76	2.42 ± 1.21	1.60 ± 0.88
1H	2.38 ± 1.20	2.62 ± 2.03	2.51 ± 0.58	0.65 ± 0.23
1D	3.87 ± 1.73	1.91 ± 0.37	1.75 ± 0.51	0.84 ± 0.35
1W	3.08 ± 2.28	3.95 ± 2.03	1.91 ± 0.80	0.63 ± 0.19
1M	2.41 ± 1.09	5.39 ± 3.68	5.78 ± 6.45	1.65 ± 1.35
1Y	12.10 ± 10.43	24.20 ± 2.78	2.05 ± 0.23	1.39 ± 1.22
R_{max} (50E)				
baseline	22.04 ± 9.37	19.42 ± 13.99	20.29 ± 13.16	11.80 ± 5.59
1H	21.15 ± 9.98	23.86 ± 17.54	22.19 ± 7.96	6.71 ± 1.15
1D	35.00 ± 17.08	20.26 ± 4.33	14.95 ± 5.64	11.51 ± 3.36
1W	26.02 ± 20.38	33.38 ± 13.64	18.89 ± 4.82	6.46 ± 2.53
1M	19.71 ± 7.14	41.02 ± 24.45	46.14 ± 51.47	13.31 ± 6.98
1Y	71.05 ± 48.08	153.41 ± 9.61	17.06 ± 2.45	14.94 ± 12.48

Table A.3.6 Summary of R_a, R_q and R_{max} (μm) of denture soft lining materials following immersion in coconut oil (CO) at 37±1°C at various time intervals, mean ± sd

R_a (CO)	**Material**			
Test period	**Vertex™Soft**	**EverSoft®**	**Molloplast-B®**	**Ufi Gel SC**
baseline	3.26 ± 0.74	0.64 ± 0.27	1.51 ± 0.09	0.47 ± 0.07
1H	3.06 ± 0.91	0.41 ± 0.19	2.57 ± 1.54	0.35 ± 0.01
1D	3.08 ± 2.27	0.54 ± 0.28	2.35 ± 0.34	0.33 ± 0.08
1W	2.47 ± 1.07	0.61 ± 0.36	2.04 ± 1.24	0.27 ± 0.10
1M	2.58 ± 0.41	0.50 ± 0.22	3.63 ± 1.42	0.32 ± 0.02
1Y	3.77 ± 1.31	0.77 ± 0.34	2.90 ± 1.41	0.61 ± 0.14
R_q (CO)				
baseline	5.69 ± 1.70	1.28 ± 0.79	2.26 ± 0.37	0.68 ± 0.21
1H	5.70 ± 1.89	0.67 ± 0.30	5.33 ± 4.75	0.51 ± 0.04
1D	5.24 ± 3.68	1.10 ± 0.92	3.73 ± 0.79	0.61 ± 0.17
1W	4.01 ± 2.27	1.59 ± 1.38	3.05 ± 1.84	0.54 ± 0.34
1M	4.51 ± 1.02	0.68 ± 0.33	8.84 ± 6.88	0.46 ± 0.04
1Y	6.09 ± 1.45	1.56 ± 1.31	6.15 ± 4.82	1.28 ± 0.45
R_{max} (CO)				
baseline	44.87 ± 12.97	14.16 ± 10.74	21.50 ± 8.10	7.89 ± 4.35
1H	52.41 ± 13.95	6.95 ± 2.85	50.07 ± 44.80	5.38 ± 1.61
1D	44.90 ± 27.32	10.42 ± 9.47	30.03 ± 8.37	7.25 ± 2.71
1W	33.44 ± 18.97	16.61 ± 12.22	24.85 ± 11.60	7.39 ± 5.33
1M	36.96 ± 6.76	6.62 ± 2.84	50.45 ± 26.43	5.44 ± 1.01
1Y	43.59 ± 10.37	15.40 ± 14.10	56.23 ± 53.11	14.65 ± 8.01

Table A.3.7 Summary of R_a, R_q and R_{max} (μm) of denture soft lining materials following immersion in HB307 (HB) at 37±1°C at various time intervals, mean ± sd

R_a (HB)	**Material**			
Test period	**Vertex™Soft**	**EverSoft®**	**Molloplast-B®**	**Ufi Gel SC**
baseline	2.37 ± 0.83	0.52 ± 0.18	1.57 ± 0.09	0.51 ± 0.11
1H	1.72 ± 0.13	0.34 ± 0.21	1.85 ± 0.37	0.43 ± 0.02
1D	1.64 ± 0.16	0.47 ± 0.29	1.72 ± 0.47	0.25 ± 0.05
1W	1.43 ± 0.26	0.51 ± 0.31	1.89 ± 0.19	0.23 ± 0.02
1M	1.24 ± 0.26	0.82 ± 0.19	2.44 ± 0.70	0.33 ± 0.10
1Y	1.69 ± 0.47	0.79 ± 0.20	2.05 ± 0.42	0.62 ± 0.35
R_q (HB)				
baseline	3.92 ± 1.60	0.97 ± 0.43	2.02 ± 0.14	0.73 ± 0.18
1H	3.06 ± 0.50	0.52 ± 0.28	2.53 ± 0.61	0.61 ± 0.05
1D	2.69 ± 0.47	1.16 ± 1.24	2.29 ± 0.60	0.40 ± 0.12
1W	2.19 ± 0.35	0.81 ± 0.37	2.46 ± 0.24	0.32 ± 0.03
1M	1.88 ± 0.59	1.56 ± 1.23	4.06 ± 1.98	0.61 ± 0.29
1Y	2.89 ± 1.01	1.45 ± 0.29	2.74 ± 0.61	1.37 ± 0.87
R_{max} (HB)				
baseline	33.51 ± 8.54	10.66 ± 7.10	13.61 ± 2.01	6.82 ± 2.22
1H	32.93 ± 6.41	5.73 ± 1.56	22.55 ± 6.95	5.79 ± 1.11
1D	25.65 ± 5.56	6.77 ± 2.88	16.99 ± 4.38	4.92 ± 2.11
1W	19.98 ± 3.40	8.20 ± 2.56	20.72 ± 3.01	3.51 ± 0.86
1M	15.67 ± 6.67	11.93 ± 5.56	35.07 ± 18.06	8.55 ± 3.83
1Y	27.64 ± 8.26	14.56 ± 2.51	19.86 ± 5.78	16.58 ± 9.27